OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

Supplement IV-OHG

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NOTE TO THE READER

This document is the fourth in a series of supplements to the 1981 Publication *NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards* (Washington, DC: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, DHHS [NIOSH] Publication No. 81-123). The three previous supplements are as follows:

1. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 88-118, Supplement I-OHG). This document contains 35 guidelines.

2. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 89-104, Supplement II-OHG). This document contains 30 guidelines.

3. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 92-110, Supplement III-OHG). This document contains 50 guidelines.

The 62 guidelines presented here in the fourth supplement include 11 revisions of previously issued guidelines and 51 new guidelines. Readers should replace the outdated guidelines in the original 1981 publication with the revised guidelines provided here.

The 62 occupational safety and health guidelines presented here are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes (1) data on the chemical name and synoyms, cemnical and physical properties, exposure limits, and signs and symptoms of exposure, and (2) recommendations for medical monitoring, personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers to achieve sound occupational health programs.

The recommendations and information in these guidelines may be superseded as new information becomes available; readers should therefore regard these recommendations as general guidelines and should not rely on them for achieving compliance with occupational safety and health regulations.

The original three-volume set of guidelines and the first three supplements to the original guidelines are available through the National Technical Information Service (NTIS) (5285 Port Royal Road, Springfield, VA 22161 [telephone: 703-487-4650]). The third suuplement can also be ordered from the Superintendent of Documents (U.S. Government Printing Office, Washington, DC 20402-9325). The stock numbers for the U.S. Government Printing Office (GPO) and NTIS are as follows:

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZIDINE

INTRODUCTION

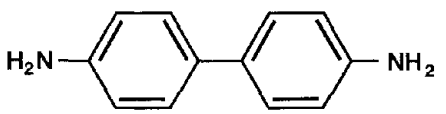
This guideline summarizes pertinent information about benzidine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{12}N_2$

- **Structure**



- **Synonyms**

1,1'-Biphenyl-4,4'-diamine, 4,4'-diaminobiphenyl, 4,4'-biphenyldiamine, 4,4'-bianiline, C.I. Azoic Diazo Component 112, Fast Corinth base B, p-diaminodiphenyl

- **Identifiers**

1. CAS No.: 92-87-5
2. RTECS No.: DC9625000
3. DOT UN: 1885 53
4. DOT label: Poison

- **Appearance and odor**

Benzidine is a white, gray-yellow, or slightly reddish crystalline solid or powder that has no odor. Benzidine is no longer manufactured commercially in the United States, although this substance is still used as an intermediate.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 184.2
2. Boiling point (at 760 mm Hg): 400°C (752°F)
3. Specific gravity (water = 1): 1.25 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of benzidine): 6.36
5. Melting point: 115°C (239°F)
6. Vapor pressure at 20°C (68°F): Quantitative data are not available, but vapor pressure is reported to be low.
7. Solubility: Slightly soluble in cold water; soluble in hot water, alcohol, and ether
8. Evaporation rate: Data not available

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- **Reactivity**

1. Conditions contributing to instability: None reported

2. Incompatibilities: Contact of benzidine with red fuming nitric acid may cause a fire.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, carbon monoxide, and benzidine vapors) may be released when benzidine is heated to decomposition.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for benzidine. Benzidine may burn, but it does not ignite readily.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to fight fires involving benzidine.

Fires involving benzidine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas. Containers of benzidine should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving benzidine. Structural firefighters' protective clothing may provide limited protection against fires involving benzidine.

EXPOSURE LIMITS

- **OSHA PEL**

Because benzidine is a recognized occupational carcinogen, the Occupational Safety and Health Administration (OSHA) standard for benzidine does not have a numerical permissible exposure limit (PEL); instead, the standard regulates the industrial use of benzidine by requiring implementation of stringent controls wherever benzidine or solid or liquid mixtures containing 0.1% or more benzidine by weight or volume are manufactured, processed, repackaged, released, handled, or stored. This standard is codified at 29 CFR 1910.1010.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers benzidine a potential human carcinogen and recommends that the above standard [29 CFR 1910.1010] be followed [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated benzidine as an A1 substance (recognized human carcinogen). The ACGIH has also assigned benzidine a Skin notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The OSHA, ACGIH, and NIOSH limits are based on the risk of bladder and other cancer associated with exposure to benzidine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to benzidine can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Benzidine is a liver toxin and a potent carcinogen in experimental animals; in carcinogencity bioassays, this substance caused tumors of the liver, mammary gland, Zymbal gland, colon, and bladder in animals of several species. The oral LD_{50} in rats is 309 mg/kg [NIOSH 1993]. The oral LD_{50} in mice is 214 mg/kg [NIOSH 1993]. Benzidine has been tested for carcinogenicity in mice, rats, and hamsters by oral administration; in mice and rats by subcutaneous administration; and in rats by inhalation and by intraperitoneal administration. Except by

inhalation, benzidine caused increased incidences in tumors, both benign and malignant, in at least one sex of animal in all species tested. Oral administration in dogs also caused bladder cancers [IARC 1982]. With activation, benzidine is mutagenic in bacterial test systems [NIOSH 1993; IARC 1982]. The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence that benzidine is an animal carcinogen [IARC 1982].

2. *Effects on Humans:* Numerous case reports and epidemiological studies in workers from many countries, including the United States, have shown that benzidine is a potent carcinogen, causing papillomas and carcinomas of the urinary tract, and especially of the urinary bladder [IARC 1972; IARC 1982]. The latency period for benzidine tumors is 2 to 42 years, with an average latency of 16 years [Proctor et al. 1988]. In one U.S. dye manufacturing facility, bladder tumors developed in 36 workers who had been exposed to benzidine over a 45-year period (1930 to 1975) [IARC 1982]. In another group of 25 U.S. workers engaged in benzidine manufacture, 13 employees were found to have bladder tumors; all five of the workers in this group who had been exposed to benzidine for more than 15 years developed bladder tumors. Airborne benzidine concentrations at this plant were estimated to have ranged from 0.005 to 17.6 mg/m^3 [IARC 1982]. An increase in the number of sister chromatid exchanges has also been reported in workers exposed to benzidine [IARC 1982]. The International Agency for Research on Cancer has concluded that there is sufficient evidence that benzidine is a human carcinogen [IARC 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms for acute inhalation or dermal exposures have been reported. However, ingestion has caused nausea, vomiting, headache, mental confusion, dizziness, vertigo, methemoglobinemia, increase in the number of white blood cells, and Heinz bodies.

2. *Chronic exposure*: Chronic exposure to benzidine may cause blood in the urine (seen microscopically in early disease) and frequent and painful urination. The onset of bladder tumors may go undetected, and the disease may be in an advanced stage before any signs or symptoms appear. Despite aggressive treatment, tumors frequently recur.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of benzidine. Benzidine can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and thoroughly wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If particulates or vapors, mists, or aerosols of benzidine are inhaled, move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if benzidine or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve benzidine and result in worker exposures to this substance:

—Use as an intermediate in the preparation of azo dyes and pigments

—Formerly used in forensic medicine to detect blood and other substances

—In declining use in security printing and as a stiffening agent in rubber compounding

—In declining use as a laboratory reagent

The only method that is effective in controlling worker exposures to benzidine is:

—Process enclosure

This substance should only be handled in closed systems.

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to benzidine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. The physician should consider whether there exist conditions associated with increased risk, including reduced immunological competence, treatment with steroids or cytotoxic agents, pregnancy, or cigarette smoking. The medical evaluation should concentrate on the function and integrity of the bladder, kidneys, liver, skin, and blood.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is potentially exposed to benzidine. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such condi-

tions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with bladder, kidney, liver, skin, and blood diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to benzidine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benzidine on the bladder, kidneys, liver, skin and blood. OSHA requires periodic examinations annually for workers potentially exposed to benzidine [29 CFR 1910.1010]. Suggested diagnostic tests include urinalysis every month (with particular attention to the presence of occult blood), urine cytology every 6 months, and cystoscopy as indicated. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urine benzidine levels may be useful in biological monitoring to assess exposure. Average urinary benzidine concentrations in workers exposed to benzidine concentrations in the range of 7 to 11 mg/m^3 are reported to be 9 mg benzidine per liter of urine (mg/l). In workers exposed to benzidine concentrations of 140 to 400 mg/m3, urinary benzidine levels reportedly range from 100 to 200 mg/l. As a carcinogen, benzidine or its metabolites should not be detectable in urine or other physiological fluids.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to benzidine may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benzidine is determined by using a glass fiber filter coated with sulfuric acid. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. Immediately after sampling, the filter must be transferred to a vial containing 2 ml of deionized water. Analysis is conducted by gas chromatography using an electron capture detector. The limit of detection for this procedure is 4.1 mg/m^3. This method is described in Method 65 of the *OSHA Analytical Methods Manual* [OSHA 1990].

PERSONAL HYGIENE

If benzidine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water. Get medical help immediately.

Clothing contaminated with benzidine should be removed immediately and should then be discarded.

A worker who handles benzidine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where benzidine or a solution containing benzidine is handled, processed, or stored.

STORAGE

Control, handling, processing, and storing of benzidine must be performed in accordance with OSHA's standard for benzidine [29 CFR 1910.1010]. This substance should be isolated in closed systems and should be well ventilated at the points where the system is opened. Containers should be kept closed and be protected from light.

SPILLS

Treat any benzidine spill as an emergency. Preplan for benzidine spills and have a trained team ready to respond in an emergency. Cleanup personnel should be clothed and

equipped in a manner that prevents any contact with benzidine.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Benzidine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for benzidine is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of benzidine per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benzidine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Benzidine is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U021. This substance has been banned from land disposal and may be treated by incineration. Benzidine also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of benzidine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or

repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with benzidine. All skin and mucous membrane contact with benzidine should be prevented by the wearing of full-body protective clothing and gloves. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benzidine. Contact lenses should not be worn if the potential exists for benzidine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR tert-BUTYL CHROMATE

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl chromate (measured as chromate) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_8H_{18}CrO_4$

- **Structure**

  $[(CH_3)_3CO]_2CrO_2$

- **Synonyms**

  t-Butyl chromate; bis(tert-butyl)chromate; chromic acid, di-tert-butyl ester.

- **Identifiers**

  1. CAS No.: 1189-85-1
  2. RTECS No.: GB2900000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  tert-Butyl chromate is a clear, colorless liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 230.3
  2. Boiling point: Data not available
  3. Specific gravity: Data not available
  4. Vapor density (air = 1 at boiling point of tert-butyl chromate): 7.9
  5. Melting point: -5° to 0°C (23° to 32°F)
  6. Vapor pressure: Data not available
  7. Solubility: tert-Butyl chromate is miscible with water
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame may ignite the flammable liquid solution used as a carrier for shipping tert-butyl chromate.

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2. Incompatibilities: Contact of tert-butyl chromate with reducing agents and moisture should be avoided, and contact with acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur) may cause a violent reaction.

3. Hazardous decomposition products: Acrid and irritating fumes and poisonous gases may be released in a fire involving tert-butyl chromate.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to tert-butyl chromate. Other sources rate tert-butyl chromate as a dangerous fire hazard.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, sand, water spray, or foam to extinguish fires involving tert-butyl chromate.

Fires involving tert-butyl chromate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of tert-butyl chromate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if a rising sound from a venting safety device is heard or if there is discoloration of a container due to fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving tert-butyl chromate. Structural fire-fighters' protective clothing will provide limited protection against fires involving tert-butyl chromate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl chromate (measured as chromate) is 0.1 mg/m^3 as a ceiling limit. A worker's exposure to tert-butyl chromate shall at no time exceed this ceiling level. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers tert-butyl chromate a potential human carcinogen and has issued a recommended exposure limit (REL) for tert-butyl chromate (measured as hexavalent chromium) of 1 g/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl chromate (measured as chromate) a ceiling limit value of 0.1 mg/m^3, which should not be exceeded during any part of the working exposure. The ACGIH also assigns a "Skin" notation to tert-butyl chromate [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the inferred risk of cancer associated with exposure to this substance [NIOSH 1992]. The ACGIH limit is based on the risk of pulmonary changes, narcosis, and necrotic lesions of the skin associated with exposure to this substance [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to tert-butyl chromate can occur through

inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* tert-Butyl chromate is a hexavalent chromium compound. Although there are no acute toxicity data specifically for this chromate, hexavalent chromium compounds are known to cause cancer in experimental animals, including lung cancers, injection-site tumors, and cancer of the kidneys [Langard 1988]. In contact with the skin of animals, tert-butyl chromate causes necrosis of the skin at the site of contact; death caused by percutaneous absorption of lethal quantities of this substance also occurs [ACGIH 1991]. Rats exposed repeatedly for 30 to 60 minutes/day to an unspecified but lethal concentration of tert-butyl chromate and butyl alcohol showed signs of respiratory and skin irritation and behavioral changes before death [ACGIH 1991]. At autopsy, lung edema and fatty deposition in the liver were seen in these animals [ACGIH 1991]. In another study, exposure of rats to tert-butyl chromate alone (concentration not specified) caused an increase in respiratory rate and signs of mild narcosis [ACGIH 1991].

2. *Effects on Humans:* NIOSH classifies all hexavalent chromium compounds, including tert-butyl chromate, as potential occupational carcinogens. However, there is little toxicity information specifically for organic hexavalent compounds, including tert-butyl chromate. In humans, tert-butyl chromate causes acid-like burns and necrotic lesions in contact with the eyes or skin, and exposure to the vapor of this substance causes irritation of the upper respiratory tract and may lead to ulceration of the nasal septum [NJDH 1987]. Skin contact can also cause an allergic rash in sensitive individuals, and long-term exposure may lead to kidney or liver damage [NJDH 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to tert-butyl chromate include redness and inflammation of the eyes and eyelids, runny nose, sore throat, coughing, nose bleeds, nasal discharge, crusting or sores in the nose, and skin and eye burns.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to tert-butyl chromate include perforation of the nasal septum, jaundice, enlarged and tender liver, and blood, pus, or protein in the urine.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl chromate! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if tert-butyl chromate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cav-

ity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve tert-butyl chromate and lead to worker exposures to this substance:

—Use in specialty reactions as an organic source of chromium

—Manufacture of catalysts

—Use for polymerizing olefins and as a curing agent for urethane resins

The following methods are effective in controlling worker exposures to tert-butyl chromate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to tert-butyl chromate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concen-

trate on the function and integrity of the eyes, skin, respiratory tract, kidneys, and liver. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl chromate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin or respiratory allergies or findings consistent with diseases of the eyes, skin, respiratory tract, kidneys, or liver.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to tert-butyl chromate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl chromate on the eyes, skin, respiratory tract, kidney, or liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary chromium concentrations correlate well with airborne chromium concentrations and are believed to be good indicators of recent short-term exposure. A urinary chromium level of 40-50 g/liter urine, or 30 g per gram creatinine, is believed to correspond to exposure to an airborne chromium level of 0.05 mg/m3 [Baselt 1988].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to tert-butyl chromate may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne tert-butyl chromate is made using a low ash polyvinyl chloride (LAPVC) 5-micron filter. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. The sample is then treated with a carbonate/bicarbonate buffer to extract the tert-butyl chromate. Analysis is conducted by polarographic analysis using differential pulse polarography. This method has a sampling and analytical error of 0.18 and is described in the OSHA Computerized Information System [OSHA 1993] and in Method ID-103 of the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

Because tert-butyl chromate can be absorbed through the skin in toxic amounts, workers should immediately wash any affected areas with soap and water.

Clothing contaminated with tert-butyl chromate should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of tert-butyl chromate, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles tert-butyl chromate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where tert-butyl chromate or a solution containing tert-butyl chromate is handled, processed, or stored.

STORAGE

tert-Butyl chromate should be stored in an explosion-proof refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of tert-butyl chromate should be protected from physical damage and should be stored separately from reducing agents, moisture, acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur), heat, sparks, and open flame. Because containers that formerly contained tert-butyl chromate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving tert-butyl chromate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Remove all sources of heat and ignition.

3. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

4. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

5. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl chromate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  tert-Butyl chromate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of tert-butyl chromate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and that manufacture 25,000 lb or more or otherwise use 10,000 lb or more of a chromium compound per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of such compounds emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although tert-butyl chromate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addi-

tion, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of tert-butyl chromate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with tert-butyl chromate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to tert-butyl chromate permeation; however, butyl rubber and polyvinyl chloride have been tested against a chemically similar material (chromic acid) and will potentially resist permeation for periods greater than 4 but fewer than 8 hours. Since specific test data are not available for tert-butyl chromate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to tert-butyl chromate.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl chromate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl chromate. Contact lenses should not be worn if the potential exists for tert-butyl chromate exposure.

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OSHA [1993]. Computerized information system. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM OXIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium oxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CaO

- **Synonyms**

  Lime, burnt lime, calcia, calx, quicklime, pebble lime, unslaked lime

- **Identifiers**

  1. CAS No.: 1305-78-8
  2. RTECS No.: EW3100000
  3. DOT UN: 1910 60
  4. DOT label: None

- **Appearance and odor**

  Calcium oxide may take the form of odorless crystals, white or grayish-white lumps, or granular powder. The commercial material may have a yellowish or brownish tint because of its iron content.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 56.08
  2. Boiling point (760 mm Hg): 2,850°C (5,162°F)
  3. Specific gravity (water = 1): 3.32 to 3.35 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 2,572°C (4,662°F)
  6. Vapor pressure at 20°C (68°F): 0 mm Hg
  7. Solubility: Soluble in water (forms slaked lime and generates a large quantity of heat); soluble in acids, glycerol, and sugar solution; practically insoluble in alcohol.
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Moisture

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2. Incompatibilities: Contact of calcium oxide with water causes a violent reaction, and the heat liberated during this reaction may cause the ignition of combustible substances. Calcium oxide reacts violently with ethanol, liquid hydrogen fluoride, some acids, some halogens, some metal halides, some metals, and some oxides, boron trifluoride, liquid hydrofluoric acid, phosphorus pentoxide, boric oxide and calcium chloride mixtures, fluorine, chlorine trifluoride, and carbon dioxide.

3. Hazardous decomposition products: Toxic particulates (such as particles of calcium hydroxide) may be released in a fire involving calcium oxide.

4. Special precautions: When exposed to air, this substance will react with the moisture and the carbon dioxide in the air. Calcium oxide swells when moist and may burst its containers.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) for calcium oxide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Calcium oxide will not burn. Because water reacts violently with calcium oxide, it should NOT be used as an extinguishant. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium oxide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of calcium oxide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do NOT allow water to come into contact with the contents of containers. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium oxide. Structural firefighters' protective clothing may provide limited protection against fires involving calcium oxide.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium oxide is 5 mg/m^3 as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium oxide a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of eye, skin, and respiratory tract irritation associated with exposure to calcium oxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium oxide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* No published data on the effects of calcium oxide exposure in animals were available for review.

2. *Effects on Humans:* Calcium oxide causes marked irritation and corrosion of contacted tissues. The irritant and corrosive effects of exposure to calcium oxide dust are primarily a result of its alkalinity and

its heat-generating reaction when in contact with moisture [Clayton and Clayton 1981]. Addition of water to calcium oxide has generated temperatures as high as 800°C (1,472°F) [NLM 1991]. In contact with the eyes, calcium oxide causes severe burns and may cause corneal ulceration [Grant 1986; Sittig 1985]. In contact with the skin, calcium oxide causes dermatitis or corrosive burns, with desquamation and a vesicular rash [Sittig 1985]. Inhalation of the dust at a concentration of 25 mg/m^3 caused marked nasal irritation in exposed workers; however, at a concentration of 9 or 10 mg/m^3, this effect disappeared [Clayton and Clayton 1981]. Exposure to calcium oxide at unspecified concentrations causes inflammation of the respiratory passages and ulceration and perforation of the nasal septum [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium oxide can produce spasmodic blinking, tears, and adhesion of calcium oxide particles to the eyeball and the conjunctival sac; dermatitis with desquamation and a vesicular rash, ulceration, and corrosive burns; and coughing, sneezing, and inflammation of the nose and throat, bronchitis, and pneumonia.

2. *Chronic exposure:* Calcium oxide has caused ulceration and perforation of the nasal septum and severe recurrent dermatitis.

- **Emergency procedures**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium oxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium oxide and may result in worker exposures to this substance:

—Use as raw material in the preparation of chlorinated lime, bleaching powder, and calcium salts and as a binding agent in the manufacture of Portland cement, mortar, stucco, plaster, bricks, refractory material, and glass

—Use as a softening, purifying, coagulating, and suspending compound in water treatment and purification; as a neutralizer of acid waste effluents; to remove sulfur dioxide from stack gases; to treat sewage and waste from steel fabrication and chemical, pharmaceutical, and explosives manufacturing facilities; and to remove sulfur from process streams in petroleum refining

—Use in wire-drawing operation in the manufacture of iron and steel; as a promoter of iron catalysts in ammonia synthesis; in flotation of nonferrous ores and in the refining of ores to remove silica; and as a flux during metal refining and smelting

—Manufacture of aluminum, magnesium, calcium carbide, and sodium carbonate and in the synthesis of chemical and dye intermediates, paint pigments, pharmaceuticals, drilling fluids, and lubricants

—Use in Kraft pulp processing of paper, to clarify cane and beet sugar juices, and as a nutrient and/or dietary supplement and food additive

—Use in dehairing of hides in leather manufacture; in manufacture of pesticides, insecticides, and fungicides; and in cleaning operations as bleach, disinfectant, and deodorizer

The following methods are effective in controlling worker exposures to calcium oxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium oxide, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggra-

vated or may result in increased risk when a worker is exposed to calcium oxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium oxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium oxide on the eyes (especially the cornea and conjunctiva), skin, and respiratory tract. The mucosa of the nose and mouth and the nasal septum should be examined for evidence of ulceration or perforation. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium oxide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium oxide is determined by using a 0.8-micron mixed cellulose ester filter (MCEF). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 400 liters is collected. The samples are ashed with nitric and hydrochloric acids. Ionization interferences are controlled with 1,000 µg/ml potassium. Analysis is conducted by atomic absorption spectroscopy with a nitrous oxide/acetylene flame. The limit of detection for this procedure is 0.03 µg/ml. This method is described in OSHA Method No. ID-121 in the *OSHA Analytical Methods Manual* [OSHA 1985]. A similar method is described in NIOSH Method 7020 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If calcium oxide contacts the skin, particles should be removed with oil or grease before they are flushed with flooding amounts of water.

Clothing contaminated with calcium oxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium oxide, particularly its potential to cause eye, skin, and upper respiratory tract irritation and burns.

A worker who handles calcium oxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium oxide or a solution containing calcium oxide is handled, processed, or stored.

STORAGE

Calcium oxide should be stored in a cool, dry, well-ventilated area in tightly sealed, airtight containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium

oxide should be protected from physical damage and should be stored separately from water and other sources of moisture, acids, oxidizers, organic materials, other combustibles, heat, and open flame. Because containers that formerly contained calcium oxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium oxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be followed after a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of moisture.
4. Ventilate the area of the spill.
5. Do NOT use water on the spilled material; collect the spilled material and gently place it in a clean, dry container creating as little dust as possible. Cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium oxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium oxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium oxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium oxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium oxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, gauntlets, and coveralls) should be worn to prevent any skin contact with calcium oxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium oxide permeation; however, natural rubber, neoprene, and nitrile rubber have been tested against chemically similar materials (calcium hydroxide) and may provide protection for more than 8 hr. Since specific data are not available for calcium oxide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium oxide.

Goggles or face shields should be worn during operations in which calcium oxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium oxide. Contact lenses should not be worn if the potential exists for calcium oxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAMPHOR, SYNTHETIC

INTRODUCTION

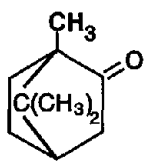
This guideline summarizes pertinent information about synthetic camphor for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{16}O$

- **Structure**



- **Synonyms**

2-Camphanone, 2-bornanone, gum camphor, Formosa camphor, Japan camphor, matricaria camphor, 1,7,7-trimethylbicyclo(2.2.1)-2-heptanone, laurel camphor, 2-keto-1,7,7-trimethylnorcamphane

- **Identifiers**

1. CAS No.: 76-22-2
2. RTECS No.: EX1225000
3. DOT UN: 2717 32
4. DOT label: Flammable Solid

- **Appearance and odor**

Camphor is a colorless or white crystalline mass with a penetrating, aromatic odor and slightly bitter, cooling taste. The odor threshold of camphor is reported to be 0.079 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 152.23
2. Boiling point (760 mm Hg): 204°C (399.2°F) sublimes
3. Specific gravity (water = 1): 0.99 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of camphor): 5.2
5. Melting point: 179.8°C (355°F)
6. Vapor pressure at 20°C (68°F): 0.18 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; soluble in aniline, nitrobenzene, carbon disulfide, tetralin, decalin, methylhexalin, petroleum ether, the higher alcohols, and fixed and volatile oils. Also soluble in concentrated mineral acids in phenol, liquid ammonia, and liquid sulfur dioxide.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of camphor with strong oxidizing agents such as potassium permanganate and chromic anhydride may form explosive mixtures.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving camphor.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) for camphor.

1. Flash point: 66°C (150°F) (closed cup)

2. Autoignition temperature: 466°C (871°F)

3. Flammable limits in air (% by volume): Lower, 0.6; upper, 3.5

4. Extinguishant: Use dry chemical, sand, water spray, fog, or standard foam to fight fires involving camphor. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving camphor should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of camphor may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving camphor. Structural firefighters' protective clothing may provide limited protection against fires involving camphor.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for camphor is 2 mg/m^3 (approximately 0.3 ppm) of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for camphor of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned camphor a threshold limit value (TLV) of 2 ppm (12 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 3 ppm (19 mg/m^3) for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 min [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of irritation associated with exposure to camphor.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to camphor can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Camphor is a central nervous system toxin in animals. The toxicity can vary depending on whether the racemate or isomers were studied: *dl*, *d*, *l*, or β [NIOSH 1991]. The lethal concentration for mice exposed to camphor for 3 hr ranged from 400 to 1,760 mg/m^3 [Izmerov et al. 1982]. Although camphor is only slowly absorbed from subcutaneous or intramuscular injection sites, absorption from mucous membranes and alimentary tract is rapid [NLM 1991]. The lowest lethal dose by subcutaneous administration in the mouse is 2,200 mg/kg while the lowest lethal oral dose in rabbits is 2 g/kg [NIOSH 1991]. Animals acutely poisoned may exhibit mydriasis, convulsions, and central nervous system stimulation before death [NIOSH 1991]. Death by asphyxiation occurred in dogs that ingested a lethal amount (9 to 14 g) [NLM 1991]. Prolonged (duration not specified) inhalation of camphor at a concentration of 6 mg/m^3 caused injury described as severe to experimental animals; at autopsy, congestion and edema of the gastrointestinal tract, kidneys, and brain were seen [ACGIH 1991]. Subcutaneous injection of camphor in rats over an 18-month period caused no increase in the incidence of tumors, but the addition of croton oil (a known cancer promoter) to the camphor mixture caused carcinomas in 2 of 110 treated mice [ACGIH 1991].

2. *Effects on Humans:* Camphor is irritating to the nose and throat of exposed individuals; at high concentrations, it is a central nervous system stimulant and convulsant [Proctor et al. 1988]. One fatal case of camphor poisoning discussed in the literature resulted from inhalation of the vapor of heated camphor. In this case, the major symptom of overexposure was marked rigidity of the jaw muscles [ACGIH 1991]. Adults have survived ingested doses up to 1.5 grams while doses of <1 gram have been fatal. A fetal death resulted when a pregnant mother ingested camphor. Necropsy revealed severe atelectasis and central neuronal necrosis in the fetus [NLM 1991]. Serious acute overexposures to unspecified concentrations or ingested amounts can cause irritation, anxiety, headache, nausea, vomiting, excitement, restlessness, dyspnea, dizziness, confusion, delerium, hallucinations, tremors, twitching of facial muscles, spasticity, convulsions, and coma [Proctor et al. 1988; ACGIH 1991]. Death can result from respiratory failure or status epilepticus [NLM 1991]. A study of workers employed in a synthetic camphor packaging plant revealed that daily exposure (5 days/week for up to 10 months) did not cause irritation of the eyes and nose or loss of the sense of smell if the camphor concentration was maintained at or below 2 ppm [ACGIH 1991]. At this or higher concentrations, however, exposure caused eye and nose irritation and loss of the ability to smell [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Camphor can cause irritation of the eyes, nose, and upper respiratory tract; anxiety; headaches; nausea; vomiting; excitement; restlessness; dyspnea; confusion; dizziness; twitching of facial muscles; spasticity; convulsions; and coma.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to camphor include irritation of the eyes and nose and loss of the sense of smell.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if camphor or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of the possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve camphor and may result in worker exposures to this substance:

—Mixing and packaging of cellulose nitrate for photographic film, cosmetics (perfumes), embalming fluid, pharmaceuticals, insect repellants, and mildew repellants

—Manufacture of plastics (especially celluloids), explosives, and incense

—Use as a plasticizer for cellulose esters and ethers, as a preservative in pharmaceuticals and cosmetics, in liniments for lumbago and related disorders, as a respiratory and circulatory stimulant, and as a topical anti-infective, counter-irritant antipruritic, and anesthetic

—Use as a catalyst or chemical intermediate in manufacturing of cumene and sulfuryl chloride, in mixing and blending of certain lacquers and varnishes, and as an odorant-flavorant during preparation and packaging of certain foods, toothpaste and powders, depilatories, deodorants, and tobacco

—Use in dentistry for the treatment of infected root canals

The following methods are effective in controlling worker exposures to camphor, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1991]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations

should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to camphor, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to camphor at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with convulsive disorders or diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to camphor exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of camphor on the central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for camphor.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne camphor is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 25 liters is collected. The samples are desorbed with carbon disulfide methanol (99:1). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.05 mg per sample. This method is described in NIOSH Method No. 1301, *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If camphor contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with camphor should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of camphor, particularly its potential to be an irritant of the eyes, respiratory tract, and skin.

A worker who handles camphor should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where camphor or a solution containing camphor is handled, processed, or stored.

STORAGE

Camphor should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard

[29 CFR 1910.1200]. Containers of camphor should be protected from physical damage and should be stored separately from potassium permanganate, chromic anhydride, other oxidizers, heat, sparks, and open flame. Because containers that formerly contained camphor may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving camphor, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Cover area of the spill with dry sand, vermiculite, or other noncombustible absorbent material, mix well, and place into closed containers for later disposal. Keep container tightly sealed.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) regulatory requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Camphor is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of camphor; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of camphor emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although camphor is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 CFR 355.40], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information on their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of camphor exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use

only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with camphor. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to camphor permeation, although some sources recommend the use of rubber. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to camphor.

If camphor is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which camphor might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with camphor. Contact lenses should not be worn if the potential exists for camphor exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBARYL

INTRODUCTION

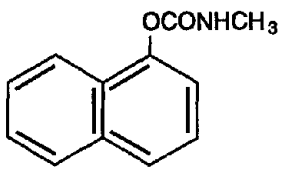
This guideline summarizes pertinent information about carbaryl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{11}NO_2$

- **Structure**



- **Synonyms**

Sevin, 1-naphthyl n-methylcarbamate, alpha-naphthyl n-methylcarbamate, methylcarbamic acid-1-naphthyl ester

- **Identifiers**

1. CAS No.: 63-25-2
2. RTECS No.: FC5950000
3. DOT UN: 2757 55
4. DOT label: None

- **Appearance and odor**

Carbaryl is an odorless white, gray, or colorless solid. This substance is a carbamate pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 201.22
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.23 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 142°C (287.6°F)
6. Vapor pressure at 25°C (77°F): <0.00004 mm Hg
7. Solubility: Nearly insoluble in water; moderately soluble in dimethylformamide, acetone, isophorone, and cyclohexanone.
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Unstable above 70°C (148°F); hydrolyzes in alkalies

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

2. Incompatibilities: Contact of carbaryl with strong oxidizers may cause fires and explosions. Carbaryl is also incompatible with strongly alkaline pesticides.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, methylamine, and carbon monoxide) may be released in a fire involving carbaryl.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to carbaryl. This substance is not flammable, although other constituents of carbaryl formulations may be flammable or combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinquishant that is suitable for the materials involved in the surrounding fire.

Fires involving carbaryl should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbaryl formulations may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbaryl. Chemical protective clothing that is specifically recommended for carbaryl may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving carbaryl.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbaryl is 5 mg/m^3 as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for carbaryl is 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbaryl a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of teratogenic, systemic, and other effects associated with exposure to carbaryl, and the NIOSH limit is based on the risk of central nervous system and reproductive effects associated with exposure to carbaryl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbaryl can occur through inhalation, eye and skin contact, percutaneous absorption, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Carbaryl inhibits cholinesterase enzyme activity in the central, autonomic, and peripheral nervous systems. This chemical was mildly irritating to exposed rabbit eyes and severely irritating to rabbit skin following a 24-hr contact period [NIOSH 1992b]. Guinea pigs showed a weak skin sensitization reaction to carbaryl [Carpenter et al. 1961]. The dermal LD_{50} is 4,000 mg/kg for rats and 2,000 mg/kg for rabbits [NIOSH 1992b]. Goats acutely drenched with carbaryl developed anorexia, diarrhea, dullness, weakness, frothing, nasal discharge, recumbency, and death. Histopathology of necropsied tissues revealed hyperemia of the CNS, heart, liver, and kidney plus myocardial and neuronal degeneration [NLM 1992]. The lowest reported oral LD_{50} for mice is 128 mg/kg, and for rats it is 230 mg/kg [NIOSH 1992b]. Dogs were given a single

oral dose of carbaryl (250, 375, or 500 mg/kg); animals in the two higher dose groups showed signs of nervous system stimulation: lacrimation, excessive salivation, muscular twitching, incoordination, vomiting, defecation, and urination [Carpenter et al. 1961]. In the dogs given 375 mg/kg carbaryl, red blood cell cholinesterase activity was depressed by 24% to 33% [Carpenter et al. 1961]. Rats that received doses ranging from 7 to 70 mg/kg for up to 12 months developed marked functional and structural changes of the pituitary gland plus impairment of thyroid and gonadal function [IARC 1976]. Long-term exposure of pigs resulted in the induction of a progressive structural neuromyopathy that was not acutely reversible with atropine [NIOSH 1992b]. Male rats exposed to 200 mg/kg three times a week for 13 weeks did not develop adverse reproductive effects, but doses of 70 mg/kg (dosing schedule undefined) for 1 year caused reduced sperm motility and alterations in spermatogenesis [NIOSH 1992b]. Female rats exposed to a total dose of 1,370 mg/kg over 39 weeks developed menstrual cycle changes, and exposure of other rats to 5,475 mg/kg over 52 weeks caused uterine, cervix, vaginal, ovarian, and fallopian tube alterations [NIOSH 1992b]. Carbaryl has not been shown to be teratogenic at doses below those causing maternal toxicity [Proctor et al. 1988]. Carbaryl is a mutagen in a wide variety of in vitro and in vivo tests [NIOSH 1992b]. Based on a review of the results of carcinogenicity bioassays in mice and rats, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of this substance in animals is inadequate [IARC 1987].

2. *Effects on Humans:* Carbaryl causes reversible cholinesterase inhibition in humans; this effect causes acetylcholine to accumulate at synapses in the nervous system, at neuromuscular junctions of the skeletal and smooth muscles, and in the secretory glands. In two separate incidents, a liquid insecticide (carbaryl/dimethoate mixture) was splashed into a person's eyes, causing transient injury to the corneal epithelium and swelling of the lids [NIOSH 1992b]. Dermal application of carbaryl to the forearm resulted in urinary excretion of 74% of the dose applied [IARC 1976]. A single oral dose of 250 mg carbaryl (approximately 2.8 mg/kg) caused the sudden onset of abdominal pain followed by profuse sweating, lethargy, and vomiting in an adult man; after treatment, this individual recovered completely. An individual who had consumed 21 g of carbaryl (500 mg/kg) recovered from acute cholinesterase inhibition but suffered weakness of the arms and legs and had electrophysiologic findings consistent with a diagnosis of peripheral neuropathy [NIOSH 1992b]. A 75-year-old man who had excessive long-term exposure to carbaryl recovered from cholinesterase inhibition when removed from exposure, but sleep apnea and peripheral neuropathy appeared as late clinical features [NIOSH 1992b]. A group of 59 workers exposed for 19 months to carbaryl concentrations ranging from 0.23 to 31 mg/m^3 showed no overt signs or symptoms of carbamate poisoning, although their red blood cell cholinesterase activity was slightly depressed [Proctor et al. 1988]. Testicular dysfunction and abnormalities in the shape of sperm have been reported in carbaryl-exposed workers [Schrag and Dixon 1985; Wyrobek et al. 1980, 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbaryl-induced chloinesterase inhibition can cause nausea, vomiting, abdominal cramps, and diarrhea; excessive sweating and salivation; lethargy and weakness; runny nose and a sensation of tightness in the chest; contracted pupils, blurred vision, tearing, and pain in the eyes; loss of coordination, tremors, and slurring of speech; increasingly difficult respiration, convulsions, and coma. If the poisoning is severe, death from respiratory failure may follow.

2. *Chronic exposure:* Carbaryl has induced headache, memory loss, anorexia, weight loss, proximal muscle weakness, fasciculations, cramps, sleep apnea, and peripheral neuropathy.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbaryl or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** induce vomiting if carbaryl has been mixed with a petroleum distillate such as kerosene or diesel fuel.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The use of carbaryl as a molluscicide, acaricide, and insecticide (for fruits, vegetables, cotton, tobacco, ornamental trees, livestock, poultry, and pets) may result in worker exposure to this chemical.

The following methods are effective in controlling worker exposures to carbaryl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) period-

ically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to carbaryl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the red blood cell cholinesterase activity.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbaryl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with cholinesterase inhibition.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbaryl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbaryl on red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. A pre-exposure blood cholinesterase concentration should be obtained for each worker so that the postexposure concentration may be expressed as a percentage of that subject's normal cholinesterase activity. A postexposure blood cholinesterase concentration that is less than 70% of normal is considered indicative of excessive exposure to carbaryl. Although the relationship between airborne concentrations of carbaryl and urinary concentrations of 1-naphthal has not been established, urinary concentrations of 1-naphthal in excess of 4 mg/liter urine may reflect overexposure to carbaryl.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbaryl is determined by an OSHA versatile sampler (OVS-2) containing two sections of XAD-2 resin (270/140-mg sections, 20/60 mesh) and a glass fiber filter. Sampling tubes can be obtained from OSHA's Salt Lake City Analytical Laboratory. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 60 liters is collected. The samples are extracted with acetonitrile. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. The limit of detection for this procedure is 0.08 mg/m^3. This method is described in Method No. 63, OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If carbaryl contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing contaminated with carbaryl should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbaryl, particularly its potential to cause cholinesterase inhibition.

A worker who handles carbaryl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbaryl or a solution containing carbaryl is handled, processed, or stored.

STORAGE

Carbaryl should be stored in a cool, dry, continuously ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbaryl should be protected from physical damage and should be stored separately from strong oxidizers, strongly alkaline pesticides, heat, sparks, and open flame. Because containers that formerly contained carbaryl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbaryl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the carbaryl for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbaryl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbaryl is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of carbaryl per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbaryl emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity,

reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbaryl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbaryl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, full-body coveralls, and impervious footwear) should be worn to prevent repeated or prolonged skin contact with carbaryl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by carbaryl and may provide protection for more than 4 but fewer than 8 hr: natural rubber, neoprene, nitrile rubber, and polyvinyl chloride.

If carbaryl is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbaryl might contact the eyes (e.g., through splashes of carbaryl-containing formulations). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbaryl. Contact lenses should not be worn if the potential exists for carbaryl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROBENZENE

INTRODUCTION

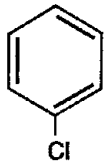
This guideline summarizes pertinent information about chlorobenzene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_6H_5Cl

- **Structure**



- **Synonyms**

  Monochlorobenzene, MCB, phenyl chloride, chlorobenzol, benzene chloride

- **Identifiers**

  1. CAS No.: 108-90-7
  2. RTECS No.: CZ0175000
  3. DOT UN: 1134 27
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Chlorobenzene is a colorless to yellowish liquid with a mild, aromatic, almond-like odor. The odor threshold of chlorobenzene is 0.21 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 112.6
  2. Boiling point (760 mm Hg): 131° to 132°C (267.8° to 270°F)
  3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chlorobenzene): 3.9
  5. Melting point: -45°C (-49°F)

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6. Vapor pressure at 20°C (68°F): 8.8 mm Hg

7. Solubility: Insoluble in water; soluble in alcohol, benzene, chloroform, and ether

8. Evaporation rate (ether = 1): 8.2

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of chlorobenzene with strong oxidizers, dimethyl sulfoxide, powdered sodium, phosphorus trichloride and sodium, or silver perchlorate causes fire, explosion, or a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chlorobenzene.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to chlorobenzene.

1. Flash point: 27.8°C (82°F)

2. Autoignition temperature: 593°C (1,099°F)

3. Flammable limits in air (% by volume): Lower, 1.3; upper, 9.6

4. Extinguishant: Use carbon dioxide, dry chemical, water spray, or standard foam to fight fires involving chlorobenzene.

Fires involving chlorobenzene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of chlorobenzene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorobenzene. Structural firefighters' protective clothing may provide limited protection against fires involving chlorobenzene.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chlorobenzene is 75 ppm (350 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for chlorobenzene [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorobenzene a threshold limit value (TLV) of 10 ppm (46 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of liver and other effects associated with exposure to chlorobenzene [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorobenzene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to chlorobenzene causes irritation, narcosis, and liver and kidney damage. In contact with the eyes of rabbits or skin of guinea pigs, chlorobenzene caused a moderate degree of irritation [ACGIH 1991]. Rats, rabbits, and guinea pigs exposed to chlorobenzene at a concentration of 1,000 ppm for 7 hr/day, 5 days/week for 44 days showed signs of lung, liver, and kidney damage; however, exposure to a 475-ppm concentration on the same regimen caused only slight liver damage in one species [Hathaway et al. 1991; ACGIH 1991]. Cats exposed to an 8,000-ppm concentration of chlorobenzene for 30 min showed signs of severe narcosis and died 2 hr after cessation of exposure; however, cats survived exposure to a 660-ppm concentration for 1 hr [Hathaway et al. 1991]. Acutely poisoned animals showed signs of eye and nose irritation and narcosis [Hathaway et al. 1991]. The oral LD_{50} in rats is 2,290 mg/kg, and the lowest lethal concentration in mice is 15 g/m^3 [NIOSH 1993]. In gavage studies of rats and mice administered chlorobenzene 5 days/week for 91 days, dose-dependent necrosis of the liver, degeneration or focal necrosis of the proximal tubules of the kidney, and myeloid or lymphoid depletion of the spleen, bone marrow, and thymus were seen at doses of 250 mg/kg/day or greater in both sexes [Hathaway et al. 1991]. In 2-year gavage studies of male and female rats and mice, male rats administered chlorobenzene doses of 120 mg/kg had a slight but statistically significant increase in neoplastic nodules of the liver. No increase in the incidence of liver tumors was seen in the mice or the female rats [Hathaway et al. 1991].

2. *Effects on Humans:* Exposure to chlorobenzene at a concentration of 200 ppm causes eye and nose irritation, and exposure to higher concentrations causes central nervous system depression. In contact with the skin for brief exposures, liquid chlorobenzene causes only mild irritation; however, prolonged or repeated contact can lead to burns of the skin [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to chlorobenzene may cause redness and inflammation of the eyes and eyelids, runny nose, sore throat, redness and irritation of the skin, headache, dizziness, drowsiness, incoherence, ataxia, loss of consciousness, twitching of the extremities, deep and rapid respiration, and irregular heartbeat. Respiratory arrest may follow.

2. *Chronic exposure:* Long-term exposure to chlorobenzene may cause chronic central nervous system depression: headache, dizziness, and somnolence. Based on effects seen in animals, chronic exposure may cause elevated liver enzymes, enlarged and tender liver, and blood, pus, or protein in the urine. Prolonged or repeated skin contact may cause skin burns.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of chlorobenzene. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chlorobenzene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorobenzene and may result in worker exposures to this substance:

—Use as a solvent for paints, adhesives, polishes, waxes, and natural rubber, and as a solvent carrier for methylene diisocyanate

—Use as a dry-cleaning agent

—Manufacture of phenol, o- and p-chloronitrobenzene, aniline, DDT, and pharmaceuticals

The following methods are effective in controlling worker exposures to chlorobenzene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chlorobenzene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, central nervous system, liver, eyes, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is

exposed to chlorobenzene at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory or central nervous system, liver, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorobenzene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorobenzene on the respiratory or central nervous system, liver, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although chlorobenzene or its metabolites can be detected in the blood or adipose tissue of exposed individuals, no biological monitoring test acceptable for routine use has yet been developed for chlorobenzene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorobenzene is determined by using a coconut shell solid sorbent tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 40 liters is collected. The samples are then desorbed with carbon disulfide to extract the chlorobenzene. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg/sample. This method is described in NIOSH Method No. 1003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If chlorobenzene contacts the skin, workers should flush the affected areas immediately with plenty of water, followed by washing with soap and water.

Clothing contaminated with chlorobenzene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chlorobenzene, particularly its potential to be irritating to the eyes and skin.

A worker who handles chlorobenzene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorobenzene or a solution containing chlorobenzene is handled, processed, or stored.

STORAGE

Chlorobenzene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of chlorobenzene should be protected from physical damage and should be stored separately from oxidizers, dimethyl sulfoxide, silver perchlorate, other incompatible chemicals, heat, sparks, and open flame. Only nonsparking tools may be used to handle chlorobenzene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained chlorobenzene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorobenzene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small dry spills, use a clean, nonsparking shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the chlorobenzene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Chlorobenzene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for chlorobenzene is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more of chlorobenzene per calendar year or otherwise use 10,000 lb or more of chlorobenzene per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorobenzene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Chlorobenzene is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U037. It is approved for land disposal as long as the concentration of chlorobenzene in the waste or treatment residual does not exceed 5.7 mg/kg. Chlorobenzene also may be disposed of in an

organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorobenzene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with chlorobenzene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material have demonstrated greater than 8 hr of resistance to breakthrough under continuous contact: Viton, Barricade, and Responder. Polyvinyl-alcohol and Teflon have shown resistance to breakthrough between 4 and 8 hr.

If chlorobenzene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chlorobenzene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chlorobenzene. Contact lenses should not be worn if the potential exists for chlorobenzene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROBENZYLIDENE MALONONITRILE

INTRODUCTION

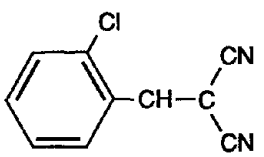
This guideline summarizes pertinent information about o-chlorobenzylidene malononitrile for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_5ClN_2$

- **Structure**



- **Synonyms**

CS; OCBM; (o-chlorobenzal)malononitrile; beta,beta-dicyano-o-chlorostyrene

- **Identifiers**

1. CAS No.: 2698-41-1
2. RTECS No.: OO3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

o-Chlorobenzylidene malononitrile is a white, crystalline solid with a pepper-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 188.6
2. Boiling point (760 mm Hg): 310° to 315°C (590° to 599°F)
3. Specific gravity (water = 1): Greater than 1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-chlorobenzylidene malononitrile): 6.5
5. Melting point: 95° to 96°C (203° to 205°F)
6. Vapor pressure at 20°C (68°F): 0.000034 mm Hg
7. Solubility: Insoluble in water; soluble in acetone, benzene, ethyl acetate, dioxane, and methylene chloride.
8. Evaporation rate: Data not available

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- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact of o-chlorobenzylidene malononitrile with strong oxidizers causes a violent reaction.

3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine, cyanide, and nitrogen oxides) may be released in a fire involving o-chlorobenzylidene malononitrile.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to o-chlorobenzylidene malononitrile.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: No information is available on the appropriate extinguishant to use for a fire involving o-chlorobenzylidene malononitrile.

Fires involving o-chlorobenzylidene malononitrile should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorobenzylidene malononitrile.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for o-chlorobenzylidene malononitrile is 0.05 ppm parts of air (0.4 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.4 mg/m^3) as a ceiling limit. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned a ceiling limit value of 0.05 ppm (0.39 mg/m^3), which should not be exceeded during any part of the working exposure. The ACGIH has also assigned a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The OSHA, NIOSH, and ACGIH limits are based on the risk of eye and respiratory tract irritation associated with exposure to o-chlorobenzylidene malononitrile [54 Fed. Reg. 2457; NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorobenzylidene malononitrile can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* o-Chlorobenzylidene malononitrile is a severe lacrimator and upper respiratory tract irritant. Human eyes are more sensitive to o-chlorobenzylidene malononitrile-induced irritation than rabbit, rat, or guinea pig eyes; however, even in extreme exposures, eye injuries are superficial and reversible [Grant 1986]. The lowest lethal concentration in rats is 1,806 mg/m^3 for 45 min [NIOSH 1993]. Rats exposed to a 1800-mg/m^3 concentration of this substance for 10 min survived, but a 60-min exposure to 2,700 mg/m^3 killed all of the animals [Hathaway et al. 1991]. The most recent oral LD_{50}s reported for rats are 1,366 mg/kg (male) and 1,284 mg/kg (female) [ACGIH 1991]. Earlier studies in rats reported oral LD_{50}s ranging from 178 to 717 mg/kg [NIOSH 1993]. This substance causes systemic cyanide poisoning when animals are exposed to high doses; the mechanism of action appears to be the release of hydrocyanic acid from one or both nitriles of the malononitrile [Gosselin et al. 1984]. Mice that were injected intraperitoneally or intravenously with o-chlorobenzylidene malononitrile or were exposed

to a concentration of 20,000 mg/m^3/min of the aerosol had cyanide in their blood and urine [ACGIH 1991].

2. *Effects on Humans:* o-Chlorobenzylidene malononitrile (OCBM) is a potent lacrimator and sternutator, and a peripheral sensory irritant in humans. This substance is the active ingredient in tear gas; exposure causes an immediate, disabling irritation of the eyes and respiratory tract in humans, but no OCBM-related deaths have been reported [Grant 1986]. Exposure to an OCBM concentration of 1.5 mg/m^3 for 90 min resulted in headaches in three of four men exposed and caused nose and eye irritation in one man [ACGIH 1991; Hathaway et al. 1991]. Contact of OCBM with the skin resulted in a burning sensation that was greatly aggravated by moisture, erythema, and vesiculation resembling second degree burns were produced [Hathaway et al. 1991]. Workers handling OCBM have developed skin sensitization; the resulting dermatitis involves the arms and neck [ACGIH 1991]. Concentrations of 4.3 to 6.7 mg/m^3 could barely be tolerated when this concentration was reached gradually over a 30-min period; subjects reported conjunctivitis, involuntary closing of the eyes, burning in the throat, cough, and chest constriction [Hathaway et al. 1991]. Concentrations greater than 10 mg/m^3 are extremely irritating and have been found to be intolerable for more than 30 seconds under test conditions; the eye irritation disappeared within an hour after cessation of exposure, and respiratory effects disappeared within a few minutes [Grant 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to o-chlorobenzylidene malononitrile may cause pain and burning of the eyes, excessive tearing, conjunctivitis, involuntary closing of the eyes, excessive salivation, nausea, vomiting, nose and throat irritation, cough, chest constriction, dizziness, headache, and redness and burning of the skin with blister formation.

2. *Chronic exposure:* Chronic exposure to o-chlorobenzylidene malononitrile may cause dermatitis of the face and arms.

- **Emergency procedures:**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water

3. *Inhalation exposure:* Move victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorobenzylidene malononitrile or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorobenzyli-

dene malononitrile and may result in worker exposures to this substance:

—Manufacturing and formulation of o-chlorobenzylidene malononitrile for use as a riot control agent

The following methods are effective in controlling worker exposures to o-chlorobenzylidene malononitrile, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to o-chlorobenzylidene malononitrile, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorobenzylidene malononitrile at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorobenzylidene malononitrile exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorobenzylidene malononitrile on the eyes, skin, or respiratory tract. Current health status should be compared with the base-

line health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. o-Chlorobenzylidene malononitrile can be detected in the blood of exposed individuals; however, blood concentrations of this substance do not correlate well with airborne concentrations. Therefore, no biological monitoring test acceptable for routine use has yet been developed for o-chlorobenzylidene malononitrile.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorobenzylidene malononitrile is determined by using a polytetrafluoroethylene (FA) 1-micron filter in series with a Tenax GC tube (70/35-mg sections, 35/60 mesh). Samples are collected at a maximum flow rate of 1.5 liter/min until a maximum air volume of 90 liters is collected. The samples are desorbed with 20% methylene chloride in hexane. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. The limit of detection for this procedure is approximately 0.3 µg/sample. This method is described in NIOSH Method P&CAM 304 of the *NIOSH Manual of Analytical Methods* [NIOSH 1977].

PERSONAL HYGIENE

If o-chlorobenzylidene malononitrile contacts the skin, workers should flush the affected areas immediately with plenty of water, and then wash with soap and water.

Clothing contaminated with o-chlorobenzylidene malononitrile should be removed immediately; provisions should be made for safely removing this chemical from these articles.

A worker who handles o-chlorobenzylidene malononitrile should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where o-chlorobenzylidene malononitrile is handled, processed, or stored.

STORAGE

o-Chlorobenzylidene malononitrile should be stored in a cool, dry, well-ventilated area or in a refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorobenzylidene malononitrile should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained o-chlorobenzylidene malononitrile may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorobenzylidene malononitrile, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.
5. For large spills, build dikes far ahead of the spill to contain the o-chlorobenzylidene malononitrile for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorobenzylidene malononitrile is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-chlorobenzylidene malononitrile; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorobenzylidene malononitrile emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorobenzylidene malononitrile is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-chlorobenzylidene malononitrile exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergency situations. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with o-chlorobenzylidene malononitrile. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommenda-

tions, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-chlorobenzylidene malononitrile permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-chlorobenzylidene malononitrile.

If o-chlorobenzylidene malononitrile is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorobenzylidene malononitrile might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorobenzylidene malononitrile. Contact lenses should not be worn if the potential exists for o-chlorobenzylidene malononitrile exposure.

REFERENCES CITED

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROPICRIN

INTRODUCTION

This guideline summarizes pertinent information about chloropicrin for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CCl_3NO_2

- **Synonyms**

  Nitrotrichloromethane, trichloronitromethane, nitrochloroform, Chlor-o-pic, Acquinite, Microlysin, Pic-fume, Profume A, Dolochlor, Larvacide 100

- **Identifiers**

  1. CAS No.: 76-06-2
  2. RTECS No.: PB6300000
  3. DOT UN: 1580 56 (liquid chloropicrin)
  4. DOT label: Poison B

- **Appearance and odor**

  At room temperature, chloropicrin is a noncombustible, oily, colorless liquid with an intense and penetrating odor. The odor threshold reported for chloropicrin is 1.1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 164.4
  2. Boiling point (760 mm Hg): 112°C (234°F)
  3. Specific gravity (water = 1): 1.66 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chloropicrin): 5.7
  5. Melting point: -64°C (-83°F) (solidifies)
  6. Vapor pressure at 20°C (68°F): 20 mm Hg
  7. Solubility: Nearly insoluble in water; soluble in ether, benzene, absolute alcohol, acetic acid, carbon tetrachloride, acetone, methyl alcohol, and carbon disulfide.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, friction, or strong impact may cause chloropicrin to detonate.
  2. Incompatibilities: Contact of chloropicrin with strong oxidizers may cause fires or explosions. Chloropicrin also reacts violently with aniline in the presence of heat, alcoholic sodium hydroxide, sodium methoxide, and propargyl bromide.

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3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, chlorine, and carbon monoxide) may be released when chloropicrin is heated to decomposition.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloropicrin; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving chloropicrin should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloropicrin may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloropicrin. Chemical protective clothing that is specifically recommended for chloropicrin may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloropicrin.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chloropicrin is 0.1 ppm (0.7 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for chloropicrin [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloropicrin a threshold limit value (TLV) of 0.1 ppm (0.67 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of severe eye, skin, and respiratory irritation with chloropicrin exposure [NIOSH 1992]. The ACGIH limit is based on the risk of severe eye and pulmonary effects associated with exposure to chloropicrin [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloropicrin can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloropicrin is a severe eye, mucous membrane, and lung irritant; it is particularly injurious to the small and medium-size bronchi. The oral LD_{50} in rats is 250 mg/kg, and the LC_{50} in the same species is 14.4 ppm for 4 hours [NIOSH 1993]. Acute poisoning causes pulmonary congestion, hemorrhage, edema, and tissue infiltration [ACGIH 1991]. Rats inhaling chloropicrin for longer test periods (duration unspecified) developed kidney, liver, and muscle damage [ACGIH 1991]. In mice, exposure to a 9-ppm concentration of chloropicrin in air caused a 50-percent decrease in respiratory rate (with ulceration and necrosis of the respiratory tract lining) and moderate lung damage [Hathaway et al. 1991]. A National Cancer Institute bioassay for carcinogenicity in rats and mice administered chloropicrin by gavage yielded inconclusive results [Clayton

and Clayton 1981]. Chloropicrin is weakly mutagenic in bacterial test systems [Hayes and Laws 1991].

2. *Effects on Humans:* Chloropicrin is a lacrimator and a severe irritant of the respiratory system in humans; it also causes severe skin irritation on contact. Chloropicrin was formerly used as a war gas; the gastrointestinal effects associated with exposure caused it to be called "vomiting gas" [Genium 1990]. Splashed into the eye, chloropicrin has caused corneal edema and liquification of the cornea [NLM 1993]. Exposure to a chloropicrin concentration of 15 ppm cannot be tolerated for more than 1 minute, and exposure to 4 ppm for a few seconds is temporarily disabling because it causes severe eye and respiratory irritation [Hathaway et al. 1991]. Exposure to 0.3 to 0.37 ppm chloropicrin for 3 to 30 seconds causes tearing and eye pain, and this substance is also a severe skin irritant [ACGIH 1991; Clayton and Clayton 1981]. Exposure to a 15-ppm concentration of chloropicrin for a few seconds causes respiratory tract injury [Clayton and Clayton 1981]. In humans, exposure to 119 ppm in air for 30 minutes is lethal; death is caused by pulmonary edema [Hathaway et al. 1991]. Twenty-seven workers in a cellulose factory who were exposed to a high (not further specified) concentration of chloropicrin for 3 minutes developed pneumonitis after 3 to 12 hours of irritating coughing and difficulty in breathing; they subsequently developed pulmonary edema and one died [NLM 1993]. Exposure to chloropicrin apparently increases an individual's susceptibility to chloropicrin intoxication on subsequent exposure [Hathaway et al. 1991; Clayton and Clayton 1981]. Sublethal exposures may cause delayed-onset pulmonary edema, and late deaths may occur from secondary infection [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to chloropicrin include severe pain and tearing of the eyes and corneal burns and opacification; burns and redness of the skin; cough, difficulty breathing, and pulmonary edema; and vertigo, nausea, and vomiting.

2. *Chronic exposure:* The signs and symptoms of repeated exposure to chloropicrin include increased susceptibility to the acute effects of this substance and damage to the lungs. Based on effects seen in animals, chronic exposure to chloropicrin may cause enlarged and tender liver, jaundice, elevated liver enzymes, and pus, blood, or protein in the urine.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of chloropicrin! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloropicrin or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

—Do *not* permit the victim to drink milk or carbonated beverages!

—Do *not* permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloropicrin and lead to worker exposures to this substance:

—Use as a fumigant on stored grains, cereals, fruits, nuts, vegetables, tobacco, floral crops, lawns, turf, and ornamentals

—Use as a soil fumigant, disinfectant, and sterilizer for the control of fungi, nematodes, and other injurious organisms

—Use as a chemical intermediate in organic synthesis of dyes (methyl violet) and as an oxidizing agent

—Use as an additive to impart a warning odor to odorless fumigants and gases

—Restricted use as a rodenticide and pesticide

—Formerly, use as a tear gas and as a chemical warfare agent

The following methods are effective in controlling worker exposures to chloropicrin, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and con-

trol work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chloropicrin, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloropicrin at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system and skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloropicrin exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloropicrin on the respiratory system or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloropicrin.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne chloropicrin is made using a midget fritted glass bubbler containing 10 milliliters of isopropanol. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. Analysis is conducted by high performance liquid chromatography with an ultraviolet detector or by gas chromatography using an electron capture detector. The limit of detection for this procedure is not known. This method is described in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

If chloropicrin contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with chloropicrin should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of chloropicrin, particularly its potential to cause severe eye and skin irritation.

A worker who handles chloropicrin should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloropicrin is handled, processed, or stored.

STORAGE

Chloropicrin should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers of chloropicrin should be protected from physical damage or shock and should be stored separately from strong oxidizers and other incompatible materials. Because containers that formerly contained chloropicrin may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloropicrin, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate atmosphere to reduce concentrations.

4. Water spray may be used to reduce vapors.

5. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the chloropicrin for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloropicrin is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloropicrin; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of chloropicrin emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although chloropicrin is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloropicrin exceeds prescribed exposure limits. Respirators

may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets) should be worn to prevent skin contact with chloropicrin. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material has been recommended for use against permeation by chloropicrin and provides protection for periods greater than 8 hours: Responder. Teflon withstands permeation by chloropicrin for greater than 4 hr but less than 8 hr.

If chloropicrin is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloropicrin might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloropicrin. Contact lenses should not be worn if the potential exists for chloropicrin exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR β-CHLOROPRENE

INTRODUCTION

This guideline summarizes pertinent information about β-chloroprene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- Formula

  C_4H_5Cl

- **Structure**

  $H_2C{=}CClCH{=}CH_2$

- **Synonyms**

  Neoprene; 2-chloro-1,3-butadiene; 2-chlorobutadiene; chloroprene

- **Identifiers**

  1. CAS No.: 126-99-8
  2. RTECS No.: EI9625000
  3. DOT UN: 1991 30
  4. DOT label: Flammable liquid

- **Appearance and odor**

  β-Chloroprene is a flammable, colorless liquid with a sharp, bitter odor. The best estimate of the odor threshold for β-chloroprene is 15 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 88.54
  2. Boiling point (760 mm Hg): 59.4°C (138.9°F)
  3. Specific gravity (water = 1): 0.958 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of β-chloroprene): 3.0
  5. Freezing point: -130 C (-202°F)
  6. Vapor pressure at 20°C (68°F): 188 mm Hg
  7. Solubility: Slightly soluble in water; miscible with ether, acetone, and benzene
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Autoxidation forms an unstable peroxide that catalyzes exothermic polymerization of the monomer.
  2. Incompatibilities: Contact of β-chloroprene with liquid or gaseous fluorine causes a violent reaction.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and hydrogen chloride) may be released in a fire involving β-chloroprene.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) for β-chloroprene.

1. Flash point: -20°C (-4°F)
2. Autoignition temperature: -15.6°C (4°F)
3. Flammable limits in air (% by volume): Lower, 4.0; upper, 20.0
4. Extinguishant: Use alcohol foam, dry chemical, carbon dioxide, or water spray to fight fires involving β-chloroprene.

Fires involving β-chloroprene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of β-chloroprene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving β-chloroprene. Chemical protective clothing that is specifically recommended for β-chloroprene may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving β-chloroprene.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for β-chloroprene is 25 ppm (90 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for β-chloroprene is 1 ppm (3.6 mg/m^3) as a ceiling limit [NIOSH 1992]. A worker's exposure to β-chloroprene shall at no time exceed this limit. However, β-chloroprene has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration.

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned β-chloroprene a threshold limit value (TLV) of 10 ppm (36 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned β-chloroprene a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of lung and skin cancer and reproductive effects associated with exposure to this substance [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to β-chloroprene can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* β-Chloroprene causes eye, skin, and respiratory tract irritation, central nervous system depression, liver damage, and reproductive/developmental effects in experimental animals. Acutely poisoned animals showed inflammation of the eyes and mucous membranes and signs of central nervous system depression before dying of respiratory failure [Hathaway et al. 1991]. The oral LD_{50} is 450 mg/kg in rats and 146 mg/kg in mice [NIOSH 1993]. The lowest lethal concentration in rats is 2,280 ppm for

4 hr [Sax and Lewis 1989]. Rats exposed 6 hr/day, 5 days/week for 4 weeks to a β-chloroprene concentration of 40 ppm showed signs of eye and skin irritation and growth depression; when the concentration was increased to 160 or 625 ppm, the animals showed loss of hair, signs of liver damage, and an increased rate of mortality [Hathaway et al. 1991]. By inhalation, chloroprene caused sterility or impotence in more than 50% of rats and mice exposed for 8 hr to concentrations ranging from 120 to 6,227 ppm (rats) or 12 to 152 ppm (mice) [ACGIH 1991; Hathaway et al. 1991]. Studies of chloroprene's embryotoxicity and teratogenicity have reported conflicting results [ACGIH 1991]. The International Agency for Research on Cancer (IARC) concluded that there was inadequate evidence in experimental animals to classify β-chloroprene's carcinogenicity [IARC 1987].

2. *Effects on Humans:* β-Chloroprene causes eye and skin irritation as well as central nervous system depression and may have reproductive, mutagenic, embryotoxic, and/or carcinogenic effects. In contact with the eyes or skin, chloroprene can cause chemical burns [Hathaway et al. 1991]. One fatality involving a worker exposed for 3 to 4 min to an unspecified chloroprene concentration in an unventilated vessel has been reported [ACGIH 1991; Hathaway et al. 1991]. Exposure to β-chloroprene concentrations ranging from 56 to greater than 334 ppm for a 1-month period was associated with hair loss, personality changes, irritability, extreme fatigue, and unbearable chest pain [Hathaway et al. 1991]. Volunteers exposed to a 973-ppm concentration of chloroprene for 15 min experienced nausea and giddiness; when these subjects performed light exercise during the exposure, they experienced these symptoms within 10 min [ACGIH 1991; Hathaway et al. 1991]. Studies of workers exposed to this substance at concentrations of 5 ppm or less report a significant increase in chromosome aberrations, and reproductive effects have been seen in male workers exposed to 0.28 to 1.94 ppm concentrations of chloroprene [Hathaway et al. 1991]. The wives of these workers also reportedly experienced a threefold excess of miscarriages [Hathaway et al. 1991]. Epidemiological studies of chloroprene-exposed workers have yielded conflicting results in the past; however, a recent study of maintenance workers showed a dose-related increase in the incidence of liver, lung, and lymphatic cancers among these workers [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to β-chloroprene may cause redness and inflammation of the eyes and eyelids, corneal necrosis, skin burns, nausea, dizziness, giddiness, personality changes, headache, irritability, reversible hair loss, insomnia, extreme fatigue, respiratory irritation, and severe chest pains.

2. *Chronic exposure:* Chronic exposure to β-chloroprene may cause effects on spermatogenesis or sperm morphology; increased risk of miscarriage; chromosome aberrations; and cancer of the lung, liver, and lymphatic system.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of β-chloroprene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if β-chloroprene or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The use of β-chloroprene in the manufacturing of neoprene and polychloroprene latex may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to β-chloroprene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to β-chloroprene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory tract, and central nervous system. Medical mon-

itoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to β-chloroprene at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, respiratory tract, or central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to β-chloroprene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of β-chloroprene on the eyes, skin, respiratory tract, or central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for β-chloroprene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne β-chloroprene is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 8 liters is collected. The sample is then treated with carbon disulfide to extract the β-chloroprene. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.03 mg/sample. This method is described in NIOSH Method No. 1002 [NIOSH 1984].

PERSONAL HYGIENE

If β-chloroprene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with β-chloroprene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of β-chloroprene, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles β-chloroprene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where β-chloroprene or a solution containing β-chloroprene is handled, processed, or stored.

STORAGE

β-Chloroprene should be stored in a cool (less than -15°C (5°F)), dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Chloroprene must be inhibited to prevent hazardous polymerization. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of β-chloroprene should be protected from physical damage and should be stored separately from fluorine, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may

be used to handle β-chloroprene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained β-chloroprene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving β-chloroprene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. For small dry spills, use a clean, nonsparking shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the β-chloroprene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

beta-Chloroprene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of β-chloroprene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or otherwise use 10,000 lb or more of β-chloroprene per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of β-chloroprene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although β-chloroprene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineer-

ing controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of β-chloroprene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent any skin contact with β-chloroprene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by β-chloroprene and have demonstrated protection for periods greater than 8 hr: Viton and polyvinyl alcohol.

If β-chloroprene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which β-chloroprene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with β-chloroprene. Contact lenses should not be worn if the potential exists for β-chloroprene exposure.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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54 Fed. Reg. 2556 [1989]. Occupational Safety and Health Administration. 29 CFR Part 1910: air contaminants; final rule. Washington, DC: U.S. Government Printing Office.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DECABORANE

INTRODUCTION

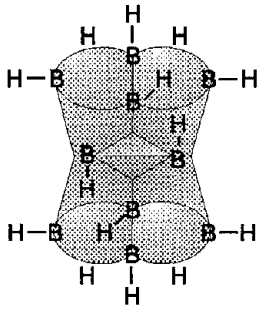
This guideline summarizes pertinent information about decaborane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$B_{10}H_{14}$

- **Structure**



- **Synonyms**

Decaboron tetradecahydride, boron hydride

- **Identifiers**

1. CAS No.: 17702-41-9
2. RTECS No.: HD1400000
3. DOT UN: 1868 34
4. DOT label: Flammable solid, poison

- **Appearance and odor**

Decaborane is a colorless to white crystalline solid with a bitter, chocolate-like odor. The median odor threshold for decaborane is 0.06 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 122.3
2. Boiling point (760 mm Hg): 213°C (416°F)
3. Specific gravity (water = 1): 0.94 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of decaborane): 4.2
5. Melting point: 99.7°C (211°F)
6. Vapor pressure at 25°C (77°F): 0.05 mm Hg
7. Solubility: Slightly soluble in cold water; soluble in

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

benzene, hexane, toluene, alcohol, and ether; very soluble in carbon disulfide

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of decaborane with oxidizers, oxygenated solvents, or dimethyl sulfoxide causes fires or explosions. In contact with carbon tetrachloride, ethers, or halocarbons, decaborane forms impact-sensitive mixtures.

3. Hazardous decomposition products: Toxic fumes (such as boron oxides) may be released in a fire involving decaborane.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to decaborane.

1. Flash point: 80°C (176°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, waterspray, or regular foam to fight fires involving decaborane.

Fires involving decaborane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of decaborane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving decaborane. Structural firefighters' protective clothing may provide limited protection against fires involving decaborane.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for decaborane is 0.05 ppm (0.3 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.3 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and a STEL of 0.15 (0.9 mg/m^3). A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day. The NIOSH REL and STEL also bear a "Skin" notation [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned decaborane a threshold limit value (TLV) of 0.05 ppm as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 0.15 ppm for periods not to exceed 15 minutes. The ACGIH also assigns decaborane a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The OSHA, NIOSH, and ACGIH limits are based on the risk of neuropathic, hepatic, and nephrotoxic effects associated with exposure to decaborane [54 Fed. Reg. 2409; NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to decaborane can occur through inhalation, ingestion, eye and skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Decaborane is toxic to the central nervous system, liver, cardiovascular system, and kidneys of experimental animals. It is toxic by all routes of exposure, and cumulative effects have been reported in rats, rabbits, and dogs [Clayton and Clayton 1981; Parmeggiani 1983]. Corneal opacities developed in mice and rats following a 4-hr exposure to a 26-ppm concentration of decaborane [Hathaway et al. 1991]. The dermal LD_{50} is 71 mg/kg in rabbits and 740 mg/kg in rats [NIOSH 1993]. The 4-hr LC_{50} is 46 ppm in rats and 12 ppm in mice [NIOSH 1993]. The oral LD_{50} is 64 mg/kg in rats and 41 mg/kg in mice [NIOSH 1993]. The manifestations of acute decaborane-induced central nervous system toxicity in rodents include hyperexcitability, restlessness, coarse head movements, generalized weakness, rigid hindquarters, absent eye reflexes, convulsive seizures, depressed breathing, and narcosis [Parmeggiani 1983; Hathaway et al. 1991]. Repeated low-dose oral exposure (3 mg/kg) to decaborane did not cause marked central nervous system effects in any test species but did cause liver and kidney damage [Hathaway et al. 1991]. Cardiovascular toxicity is manifested in dogs as slow heart rate, initial moderate elevation in blood pressure, and a final drop in blood pressure after lethal doses of decaborane are administered by any route [Hathaway et al. 1991; Parmeggiani 1983].

2. *Effects on Humans:* Decaborane causes central nervous system effects in humans. Exposure causes headaches, dizziness, drowsiness, and nausea, and severe exposure is expected to cause general weakness, incoordination, hyperexcitability, narcosis, fatigue, muscle spasms, tremors, convulsions, and unconsciousness [Hathaway et al. 1991]. The onset of symptoms may be delayed for up to 2 days. Recovery from muscle spasms may occur in 24 hours, but lightheadedness and fatigue may be present for up to 3 days [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to decaborane may include headache, dizziness, drowsiness, nausea, lightheadedness, fatigue, and incoordination. Based on effects seen in animals, exposure may cause redness and irritation of the eyes and eyelids, tremor, localized muscle spasm, and convulsions.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to decaborane may include headaches, fatigue, drowsiness, inability to concentrate, and lack of coordination. Based on effects seen in animals, chronic exposure may lead to jaundice, enlarged and tender liver, and blood, pus, or protein in the urine.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If particulates, mists, or vapors of decaborane are inhaled, move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if decaborane or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions muse be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve decaborane and lead to worker exposures to this substance:

—Use as a reducing agent in chemical synthesis and as an olefin polymerization catalyst

—Use as a vulcanizing agent in rubber manufacture and as an anti-corrosive coating for metals

—Manufacture of high-energy fuel, rocket propellants, plastics, and polymers

—Use as a stabilizer, rayon delustrant, mothproofing agent, dye-stripping agent, fluxing agent, and oxygen scavenger

The following methods are effective in controlling worker exposures to decaborane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to decaborane, a licensed health care profes-

sional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system, liver, kidneys, eyes, and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to decaborane at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system, liver, kidneys, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to decaborane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of decaborane on the central nervous system, liver, kidneys, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Borate concentrations can be measured in the serum of exposed individuals, and some sources state that serum borate concentrations greater than 20 mg/liter indicate excessive exposure. However, no biological monitoring test acceptable for routine use has yet been developed for decaborane because serum borate levels do not correlate well with airborne concentrations.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne decaborane is made using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 480 liters is collected. Analysis is conducted by inductively coupled plasma/atomic emission spectrometry. The limit of detection for this procedure is not known. Analysis is performed for total boron and then back-calculated for decaborane. This method is described in the OSHA Laboratory In-House File [OSHA 1991].

PERSONAL HYGIENE

If decaborane contacts the skin, workers should flush the affected areas immediately with 3 percent aqueous ammonia hydroxide, followed by washing with soap and water.

Clothing contaminated with decaborane should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of decaborane, particularly its potential to cause burns of the skin.

A worker who handles decaborane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, applying cosmetics, or using toilet facilities.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where decaborane or a solution containing decaborane is handled, processed, or stored.

STORAGE

Decaborane should be stored in a cool, dry, well-ventilated area in tightly sealed, weather-proof containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of decaborane should be protected from physical damage and should be stored separately from oxidizers, oxygenated solvents, dimethyl sulfoxide, heat, sparks, and open flame. Only nonsparking tools may be used to handle decaborane. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained decaborane may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving decaborane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For large liquid spills, build dikes far ahead of the spill to contain the decaborane for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility at which there are 10,000 lb or more of decaborane must comply with EPA's emergency planning requirements. (If decaborane is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 500 lb or more of decaborane are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for decaborane is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of any State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of decaborane emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although decaborane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], the EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of decaborane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent any skin contact with decaborane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to decaborane permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to decaborane.

If decaborane is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which decaborane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with decaborane. Contact lenses should not be worn if the potential exists for decaborane exposure.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PORTLAND CEMENT

INTRODUCTION

This guideline summarizes pertinent information about Portland cement (containing less than 1 percent quartz) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  Varies with composition of specific cement

- **Synonyms**

  Hydraulic cement, Portland cement silicate, cement

- **Identifiers**

  1. CAS No.: 65997-15-1
  2. RTECS No.: VV8770000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Portland cement is a finely divided gray powder containing less than 1 percent silica and composed of lime, alumina, silica, and iron oxide; small amounts of magnesia, sodium, potassium, and sulfur are also present. This substance is odorless.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: Varies with specific cement
  2. Boiling point: Not applicable
  3. Specific gravity: Not reported
  4. Vapor density: Not applicable
  5. Melting point: Not applicable
  6. Vapor pressure at 20°C (68°F): Not applicable
  7. Solubility: Insoluble in water
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: None reported
  3. Hazardous decomposition products: None reported
  4. Special precautions: None reported.

- **Flammability**

  The National Fire Protection Association has not

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assigned a fire hazard rating for Portland cement; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving Portland cement should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving Portland cement.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for Portland cement is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hour time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned Portland cement a threshold limit value (TLV) of 10 mg/m3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of physical irritation associated with exposure to Portland cement [NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to Portland cement can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Instilled intratracheally, cement dust caused an absorptive reaction in guinea pig lungs. Peritoneal nodules formed initially and then decreased progressively in size and eventually resolved spontaneously [ACGIH 1991].

2. *Effects on Humans:* Portland cement dust causes eye irritation, and prolonged or repeated contact of the dust or cement with the skin causes dermatitis [Hathaway et al. 1991]. Fifteen of 95 cement workers studied had a mild dermatitis of the hands [Hathaway et al. 1991]. A study of 2,736 Portland cement workers revealed that 5.4 percent of these workers had dyspnea, compared with a 2.7 percent prevalence among controls. There were no differences in mean pulmonary function test results between the two groups [Hathaway et al. 1991]. The mean cement dust exposure for these workers was 0.57 mg/m^3 (respirable dust), with peaks to 46 mg/m3 [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to Portland cement include physical irritation of the eyes, with redness and tearing; coughing; and redness, roughness, and scaling of the skin.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged exposure of the skin to Portland cement include coughing, expectoration, exertional dyspnea, and skin redness, blistering, burns, and, in some individuals, raised itching areas characteristic of hives.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of Portland cement is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve Portland cement and lead to worker exposures to this substance:

—Use as a binding agent in concrete and mortar

The following methods are effective in controlling worker exposures to Portland cement, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for

exposure to Portland cement, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to Portland cement at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to Portland cement exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of Portland cement on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for Portland cement.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne Portland cement is made using a tared low ash polyvinyl chloride (LAPVC) filter, 5 microns, preceded by a 10-mm nylon cyclone. A maximum air volume of 960 liters is collected at a maximum flow rate of 2 liters/min. A gravimetric analysis is then performed to measure compliance with the respirable Portland cement standard. Following this determination, an x-ray diffraction analysis of respirable quartz is done to determine compliance with the quartz standard. These methods are described in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985a], *NIOSH Occupational Exposure Sampling Strategy Manual* [NIOSH 1977] and Method No. ID-142 of the *OSHA Analytical Methods Manual* [OSHA 1985b].

PERSONAL HYGIENE

If Portland cement dust contacts the skin, workers should flush the affected areas immediately with plenty of water, and then wash with soap and water.

Clothing contaminated with Portland cement dust should be removed, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of Portland cement, particularly its potential to cause dermatitis on prolonged contact.

A worker who handles Portland cement should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where Portland cement is handled, processed, or stored.

STORAGE

Portland cement should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of Portland cement should be protected from physical damage.

SPILLS

In the event of a spill involving Portland cement, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Avoid creating dust during cleanup by using a vacuum or a wet method for cleanup.
4. For dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Portland cement is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.30] to notify the National Response Center of an accidental release of Portland cement; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of Portland cement emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although Portland cement is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of Portland cement exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been

installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, and gauntlets) should be worn to prevent prolonged skin contact with Portland cement. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to Portland cement permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to Portland cement.

Safety glasses, goggles, or face shields should be worn during operations in which Portland cement might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with Portland cement. Contact lenses should not be worn if the potential exists for Portland cement exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM CARBONATE

INTRODUCTION

This guideline summarizes pertinent information about calcium carbonate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaCO_3$

- **Synonyms**

  Aragonite, agricultural limestone, agstone, Bell mine pulverized limestone, calcite, chalk, domolite, franklin, limestone, lithographic stone, marble, Portland Stone, Sohnhofen stone

- **Identifiers**

  1. CAS No.: 1317-65-3
  2. RTECS No.: EV9580000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium carbonate is a noncombustible, odorless, white powder or colorless crystalline solid. Calcium carbonate occurs naturally in the minerals aragonite, calcite, limestone, marble, and vaterite. The two natural forms of calcium carbonate that are important commercially are aragonite and calcite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 100.09
  2. Boiling point: Not applicable
  3. Specific gravity at 20°C (68°F) (water = 1): 2.83 (aragonite); 2.71 (calcite)
  4. Vapor density: Not applicable
  5. Melting point: 825°C (1,517°F) (aragonite); 1,339°C (2,442°F) (calcite)
  6. Vapor pressure: Not applicable
  7. Solubility: Insoluble in water and alcohol; soluble in dilute acids.
  8. Evaporation rate: Not applicable

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- **Reactivity**

1. Conditions contributing to instability: None

2. Incompatibilities: Contact of calcium carbonate with acids, alum, ammonium salts, or mercury and hydrogen causes a reaction, and contact with fluorine causes ignition.

3. Hazardous decomposition products: Toxic particulates (such as calcium oxide) may be released in a fire involving calcium carbonate.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to calcium carbonate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium carbonate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium carbonate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium carbonate is 15 mg/m^3 of air (total dust) and 5 mg/m3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium carbonate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to calcium carbonate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium carbonate can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium carbonate causes moderate-to-severe irritation in contact with the tissues of animals. Instilled into rabbits' eyes, calcium carbonate caused severe irritation [NIOSH 1991]. In contact with the skin of rabbits for 24 hr, this substance caused moderate irritation [NIOSH 1991]. The oral LD_{50} in rats is 6,450 mg/kg [NIOSH 1991].

2. *Effects on Humans:* Calcium carbonate dust is a physical irritant of the eyes, nose, mucous membranes, and skin of humans. Contact of calcium carbonate dust with the eyes causes redness, pain, and inflammation of the eyelids while contact with the skin causes local irritation of moderate degree [NLM 1991]. Exposure to large amounts of the dust of this substance causes coughing, sneezing, and nasal irritation [NLM 1991]. Although chronic exposure to pure calcium carbonate does not cause pneumoconiosis, similar exposure to impure limestone (calcium carbonate) containing 3% to 20% quartz may pose a silicosis risk [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Overexposure to calcium carbonate

dust can cause irritation of the eyelids; redness, tearing, and pain in the eyes; runny nose; sneezing; and coughing. Contact with the skin causes dryness and irritation.

2. *Chronic exposure:* Although no signs or symptoms of chronic exposure to calcium carbonate have been reported, quartz contamination of limestone in excess of 2% may pose a silicosis risk.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium carbonate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** induce vomiting if calcium carbonate has been mixed with a petroleum distillate such as kerosene or diesel fuel.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve calcium carbonate and may result in worker exposures to this substance:

—Use as a neutralizing agent, filler, and extender in rubber, plastic, and paint products, and as an opacification agent in paper products

—Use in the manufacture of putty, tooth powders, antacids, whitewash, quicklime, Portland cement, dentifrices, ceramics, polishes, insecticides, inks, shoe dressings, foods, cosmetics, pharmaceuticals, antibiotics, adhesives, matches, pencils, crayons, linoleum, welding rods, and insulating compounds

—Use in removing sulfur dioxide from stack gases and as a metallurgical flux

—Use in analytical chemistry to detect and measure halogens in organic combinations and in the laboratory generation of carbon dioxide

—Use as a pigment and as a source of lime

—Use in human and veterinary medicine as an antacid.

—As a dietary supplement, as a nutrient, and as an antidiarrheal agent

The following methods are effective in controlling worker exposures to calcium carbonate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to toxic substances should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium carbonate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium carbonate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium carbonate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium carbonate on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium carbonate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the

time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

The OSHA method for determining worker exposures to airborne concentrations of calcium carbonate (total dust) is made using a tared, low-ash polyvinyl chloride filter (LAPCF) with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System as Dust, Total [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1987]. NIOSH has a similar method (Method 0500) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984a] which also involves gravimetric analysis. In the NIOSH method, samples are collected at a flow rate of 1.5 to 2 liters/min. The minimum sample volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum is 133 liters. The overall precision for the NIOSH method is 0.056.

The OSHA method for determining worker exposures to airborne concentrations of calcium carbonate (respirable fraction) is made using a tared, low-ash polyvinyl chloride filter (LAPCF) with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is held in a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 800 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System as Dust (Respirable Nuisance) [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1987]. NIOSH has a similar method (Method 0600) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984b], which also involves gravimetric analysis. In the NIOSH method, samples are collected at a flow rate of 1.7 liter/min. The minimum sample volume for an airborne concentration of 5 mg/m^3 is 75 liters, and the maximum is 1,000 liters. The overall precision for the NIOSH method ranges from 0.043 to 0.145 in laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium carbonate collects on the skin in large quantities, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium carbonate should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium carbonate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium carbonate is handled, processed, or stored.

STORAGE

Calcium carbonate should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of calcium carbonate should be protected from physical damage and should be stored separately from acids, alum, ammonium salts, fluorine, mercury, hydrogen, heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a major spill involving calcium carbonate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a major spill:

1. For small spills, vacuum or wet down the spilled material and place into waste containers for disposal.

2. For large spills, wet down the material and dike for later disposal.

3. To the extent feasible, avoid generating dust during cleanup.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium carbonate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium carbonate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium carbonate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21–261.24. Although calcium carbonate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium carbonate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with calcium carbonate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium carbonate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium carbonate.

If calcium carbonate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium carbonate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium carbonate. Contact lenses should not be worn if the potential exists for calcium carbonate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM CYANAMIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium cyanamide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaCN_2$

- **Structure**

  Ca:NCN

- **Synonyms**

  Aero-cyanamid; cyanamide, calcium salt; aero cyanamid granular; calcium carbimide; aero cyanamid special grade; Alzodef; lime-nitrogen; nitrogen lime; nitrolim, nitrolime

- **Identifiers**

  1. CAS No.: 156-62-7
  2. RTECS No.: GS6000000
  3. DOT UN: 1403 40 (not hydrated, containing more than 0.1% calcium carbide)
  4. DOT label: None (not hydrated, containing more than 0.1% calcium carbide)

- **Appearance and odor**

  Calcium cyanamide is a noncombustible, colorless, gray, or black crystalline solid or powder. No information is available on the odor of this substance. The commercial grade may contain a small amount of calcium carbide, which may produce acetylene in closed containers and vessels.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 80.11
  2. Boiling point (760 mm Hg): Sublimes at 1,150° to 1,200°C (2,102° to 2,192°F)
  3. Specific gravity (water = 1): 2.29 at 20°C (68°F)
  4. Vapor density: Data not available
  5. Melting point: 1,340°C (2,444°F)
  6. Vapor pressure: Not volatile
  7. Solubility: Decomposes in water to liberate acetylene gas and ammonia
  8. Evaporation rate: Data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Reactivity**

1. Conditions contributing to instability: Moisture

2. Incompatibilities: Contact with any form of moisture (ice, steam, moist air, water) causes calcium cyanamide to decompose, liberating acetylene and ammonia. Contact with all solvents tested also causes calcium cyanamide to decompose.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving calcium cyanamide.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to calcium cyanamide. In pure form, this substance is not combustible; however, the commercial product may contain calcium carbide, which may liberate very flammable gases and vapors on contact with moisture.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, soda ash, sand, or lime to fight fires involving calcium cyanamide. Do not use foam or water. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving calcium cyanamide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of calcium cyanamide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium cyanamide. Structural firefighters' protective clothing may not provide protection against permeation by calcium cyanamide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for calcium cyanamide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium cyanamide a threshold limit value (TLV) of 0.5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of irritation and vasomotor effects associated with exposure to calcium cyanamide [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium cyanamide can occur through inhalation, eye or skin contact, dermal absorption, or ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium cyanamide can be a severe irritant of the eyes and skin in animals. In pure water or alkaline solutions, it may polymerize to dicyandiamide, a less toxic product. When instilled into rabbits' eyes, the dust of this material was quite irritating [ACGIH 1991]. When applied as a paste to the clipped skin of rabbits under occlusion for 24 hr, a 10-g/kg dose of calcium cyanamide killed two of five rabbits; all animals survived when the dosage was reduced to 5 g/kg [ACGIH 1991]. All surviving animals developed severe skin irritation several days

after application [ACGIH 1991]. In marked contrast to the previous data concerning rabbit dermal lethality, other investigators reported the dermal LD_{50} in rabbits to be 590 mg/kg [NIOSH 1991]. The lowest lethal concentration in rats is 86 mg/m^3 for 4 hr [ACGIH 1991]. The oral LD_{50} in rats is 158 mg/kg [NIOSH 1991]. Calcium cyanamide is mutagenic in bacterial test systems [NIOSH 1991; NLM 1992]. Rats and mice fed a diet containing 63 or 126 ppm (male rats), 63 or 252 ppm (female rats), or 315 or 1,260 ppm (male and female mice) of calcium cyanamide for 2 years failed to develop tumors that were treatment related at statistically significant levels; however, some of the mice did develop hemangiosarcomas of the circulatory system, lymphomas, and leukemia [ACGIH 1991].

2. *Effects on Humans:* Calcium cyanamide is a primary irritant and sensitizer of the eyes, skin, and mucous membranes. The dust of calcium cyanamide is a primary irritant that can induce skin ulcers and be caustic to the eyes [Clayton and Clayton 1981; NLM 1992]. Skin contact with this substance also causes skin sensitization in approximately 0.5% to 1% of exposed workers [ACGIH 1991]. Inhalation of the dust can cause rhinitis, pharyngitis, laryngitis, and tracheobronchitis. Nasal septal perforation has also been reported in chronically exposed workers. Workers exposed to calcium cyanamide at unspecified concentrations may develop miosis, salivation, lacrimation, and twitching plus a transient vasomotor disturbance that can cause skin and mucous membrane flushing, nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, and low blood pressure; in severe cases, shock, coma, and death may follow [ACGIH 1991; Gosselin et al. 1984; NLM 1992]. Attacks are usually transient, lasting for 30 min to 2 hr, and the ingestion of alcohol may precipitate or intensify this syndrome [Gosselin et al. 1984]. Although an oral dose of 571 mg/kg has proved fatal in humans, the estimated total lethal dose ranges from 20 to 50 grams [NIOSH 1991; NLM 1992]. However, death occurred within 1 hr when a patient drank ethanol following ingestion of 100 mg calcium cyanamide [NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium cyanamide can cause eye irritation, runny nose, sore throat, and coughing. Itchy, reddened skin, especially on the exposed areas of the body, has been reported; continued skin contact may cause skin burns. Inhalation exposure can produce respiratory tract irritation and may cause facial and upper-body flushing, accompanied by nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, a sense of oppression in the chest, and shivering. Low blood pressure, circulatory collapse, and coma may follow in more serious exposures. These symptoms may be triggered or intensified by alcohol ingestion, and a marked intolerance to alcoholic beverages can develop.

2. *Chronic exposure:* Calcium cyanamide may cause some individuals to develop skin sensitization, with raised, reddened, and itching areas of the skin (hives). Chronic rhinitis and nasal septal perforation have also been reported in workers exposed to the dust.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! Immediately, continuously, and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium cyanamide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

   NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium cyanamide and may result in worker exposures to this substance:

—Use in the nitridation and desulfurization of steel

—Use as a raw material in the manufacture of dicyandiamide and calcium cyanide

—Use as a fertilizer and in the manufacture of nitrogen products

—Use in human medicine to treat alcoholism

—Used formerly as a defoliant, herbicide, and pesticide

The following methods are effective in controlling worker exposures to calcium cyanamide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for

exposure to calcium cyanamide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and on a history of allergies or alcohol intake. All potentially exposed workers should be warned of the adverse signs and symptoms associated with exposure to calcium cyanamide and the concomitant ingestion of alcohol.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium cyanamide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of alcohol intake or allergies and other findings consistent with skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium cyanamide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium cyanamide on the skin (including allergic sensitization) and on any vasomotor episodes that have occurred. All workers should be reminded of the adverse effects associated with concomitant exposure to calcium cyanamide and the ingestion of alcohol. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium cyanamide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium cyanamide is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If calcium cyanamide contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with calcium cyanamide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium cyanamide, particularly its potential to cause irritation of the eyes and skin.

A worker who handles calcium cyanamide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium cyanamide or a solution containing calcium cyanamide is handled, processed, or stored.

STORAGE

Calcium cyanamide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled

in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium cyanamide should be protected from physical damage and should be stored separately from moisture, calcium carbide, heat, sparks, and open flame. Because containers that formerly contained calcium cyanamide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving calcium cyanamide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Prevent any contact of calcium cyanamide with water.
6. Use nonsparking tools and equipment for cleanup.
7. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium cyanamide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium cyanamide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of calcium cyanamide per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium cyanamide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium cyanamide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium cyanamide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with calcium cyanamide. Chemically resistant gloves, boots, aprons, and gauntlets are recommended to prevent contact of the skin with this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to permeation by calcium cyanamide. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium cyanamide.

Safety glasses, goggles, or face shields should be worn during operations in which calcium cyanamide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium cyanamide. Contact lenses should not be worn if the potential exists for calcium cyanamide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM HYDROXIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium hydroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $Ca(OH)_2$

- **Synonyms**

  Bell mine, calcium hydrate, hydrated lime, caustic lime, Kemikal, slaked lime

- **Identifiers**

  1. CAS No: 1305-62-0
  2. RTECS No.: EW2800000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium hydroxide is a soft, white, powder or granule, noncombustible material with a bitter taste and no odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 74.1
  2. Boiling point (760 mm Hg): Decomposes at 580°C (1,076°F)
  3. Specific gravity (water = 1): 2.24 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 580°C (1,076°F) (loses its water)
  6. Vapor pressure: Not applicable
  7. Solubility: Soluble in water, sugar or ammonium solutions, acids, and glycerol; insoluble in alcohol
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame
  2. Incompatibilities: Explosions may result from con-

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tact of calcium hydroxide with maleic anhydride, phosphorus, nitroethane, nitromethane, nitroparaffins, or nitropropane.

3. Hazardous decomposition products: Toxic particulates (such as calcium oxide) may be released in a fire involving calcium hydroxide.

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium hydroxide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of irritation associated with exposure to calcium hydroxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium hydroxide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium hydroxide is a corrosive that affects all tissues it contacts. Direct application of an aqueous 10% calcium hydroxide solution to the central corneal surface of rabbit eyes resulted in corrosion with persisting severe irritation beyond 21 days [NLM 1992]. The oral LD_{50}s in rats and mice are 7,340 and 7,300 mg/kg, respectively [NIOSH 1991]. The eyes of rabbits were severely affected by the application of 10 mg calcium hydroxide [Grant 1986; Sax and Lewis 1989]. Rats whose drinking water contained 50 or 350 mg calcium hydroxide/liter became restless and aggressive after 2 months and showed a loss in body weight, decreased phagocyte and erythrocyte counts, and decreased hemoglobin after 3 months on this regimen. Autopsy showed inflammation of the small intestines and dystrophic changes in the stomach, kidneys, and liver of these animals [Proctor et al. 1988].

2. *Effects on Humans:* Calcium hydroxide is a tissue corrosive and one of the most common causes of corrosive chemical eye burns. Direct contact of the skin with calcium hydroxide causes skin irritation and may also lead to corrosive chemical burns [Grant 1986; Clayton and Clayton 1981]. Because calcium hydroxide slowly penetrates the skin, the degree of damage is directly related to the degree and duration of exposure [NLM 1992]. Prolonged contact of the skin with calcium hydroxide may cause skin desquamation and a vesicular rash, skin ulceration, and corrosion in some cases [Parmeggiani 1983; NLM 1992]. Ingestion of this material has caused severe pain, vomiting, tissue corrosion, perforation, and death. Survivors may develop esophageal strictures [NLM 1992]. Chronic dermatitis can also be induced by repeated exposure to this alkali [NLM 1992]. Chronic inhalation of calcium hydroxide dust is reported to have caused bronchitis and pneumonia [Parmeggiani 1983].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium hydroxide can induce redness, tearing, irritation, or corrosion of the eyes; runny nose, upper respiratory tract irritation, bronchitis, and pneumonia; and redness, rashes, irritation, or corrosion of the skin.

2. *Chronic exposure:* Calcium hydroxide can cause chronic skin dermatitis, desquamation, vesiculation, and ulceration, as well as coughing, fluid in the lungs, and difficult breathing.

- **Emergency procedure**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash

skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium hydroxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium hydroxide and may result in worker exposures to this substance:

—Manufacture of medicinal antacids, fecal deodorants, polysaccharides, mortar, plaster, whitewash, cement, and other paving and building materials

—Use as an intermediate in the production of propylene oxide and calcium hypochlorite, as a flux in iron and steel manufacture, and as a buffering agent for metals, pearls, and celluloid

—Use in lubricants, drilling fluids, fertilizers, and pesticides

—Use to dehair hides

—Use in water softening and treatment and in water-based paints

—Use in fireproofing compounds, fireproof coatings, and in soil treatment

—Use as a scrubbing and neutralizing agent in the chemical industry

—Manufacture of calcium salts, causticizing soda, and depilatories

—Use in ammonia recovery, in gas manufacture, in paper pulp manufacture, in the purification of sugar juices, as a disinfectant, as an accelerator for low-grade rubber compounds, in petrochemicals, and as a shell-forming agent in the poultry industry

The following methods are effective in controlling worker exposures to calcium hydroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to calcium hydroxide, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium hydroxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium hydroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium hydroxide on the skin and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium hydroxide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium hydroxide is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 480 liters is collected. The sample is then treated with water to extract the calcium hydroxide. Analysis is conducted by atomic absorption spectroscopy. This method has a sampling and analytical error of 0.28 and is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If calcium hydroxide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium hydroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium hydroxide, particularly its potential to cause skin burns.

A worker who handles calcium hydroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium hydroxide or a solution containing calcium hydroxide is handled, processed, or stored.

STORAGE

Calcium hydroxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium hydroxide should be protected from physical damage and should be stored separately from acidic materials, maleic anhydride, nitroethane, nitromethane, nitropropane, nitroparaffins, phosphorus, heat, sparks, and open flame. Because containers that formerly contained calcium hydroxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium hydroxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill to reduce dust concentration.
4. To the extent possible, avoid generating dust during cleanup.
5. For small spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium hydroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium hydroxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium hydroxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium hydroxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium hydroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with calcium hydroxide. Chemically resistant clothing, gloves, boots, and other protective clothing are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by calcium hydroxide and may provide protection for periods greater than 8 hr: natural rubber, nitrile rubber, and neoprene rubber. Polyvinyl chloride has also demonstrated good-to-excellent resistance when tested against calcium hydroxide.

Safety glasses, goggles, or face shields should be worn during operations in which calcium hydroxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium hydroxide. Contact lenses should not be worn if the potential exists for calcium hydroxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM SILICATE

INTRODUCTION

This guideline summarizes pertinent information about calcium silicate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaSiO_3$

- **Synonyms**

  Calcium metasilicate, wollastonite, calcium hydrosilicate, calcium monosilicate, calcium salt of silicic acid, Calflo E, Calsil, CS Lafarge, Micro-Cel, Silene EF

- **Identifiers**

  1. CAS No.: 1344-95-2
  2. RTECS No.: VV9150000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium silicate is a noncombustible, white or cream-colored, free-flowing powder that is prepared commercially from lime and diatomaceous earth; many different calcium silicates occur in nature in mineral form (e.g., wollastonite, afwillite, grammite).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 116.16
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity (water = 1): 2.9 at 20°C (68°F)
  4. Vapor density: Data not available
  5. Melting point: 1,540°C (2,804°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; forms a siliceous gel with mineral acids
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: None reported

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3. Hazardous decomposition products: None reported

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to calcium silicate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium silicate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium silicate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium silicate is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable dust) for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium silicate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on calcium silicate's local irritant properties.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium silicate can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* The toxicity of calcium silicate depends on the silica content and amount of respirable fiber in the particular calcium silicate preparation; studies in animals should be interpreted with this information in mind. Rats exposed to 10 mg/m^3 concentrations of various calcium silicate preparations, measured as respirable dust (approximately 19 to 25 mg/m^3 total dust), for 7 hr/day, 5 days/week for 224 days in a 12-month period showed no pulmonary lesions except for a few nodules in the animals exposed to the calcium silicate preparation that contained about 1% crystalline silica [ACGIH 1991]. No mesotheliomas were seen in groups of rats injected intraperitoneally with three different calcium silicate preparations [ACGIH 1991]. One experiment in rats showed a significant increase in the incidence of pleural sarcomas after wollastonite (naturally occurring calcium silicate) fibers were implanted intrapleurally [IARC 1987]. Rats, guinea pigs, and hamsters exposed for as long as 36 months to synthetic calcium silicate containing 15% asbestos at concentrations ranging from 100 to 125 million particles per cubic foot (mppcf) developed fibrosis; the authors of this study attributed the fibrosis to the asbestos in the product [ACGIH 1991].

2. *Effects on Humans:* The toxicity of calcium silicate depends on the particle size, amount of silica, the aspect ratio, and the amount of respirable fiber in the particular calcium silicate product being used; studies in humans should be interpreted with this in mind. Calcium silicate causes physical irritation when in contact with the eyes, skin, or upper respiratory tract of exposed workers. In vitro toxicity studies of calcium silicate insulation materials demonstrated equivocal hemolysis potential (one greater versus one less)

but less cytotoxicity than asbestos [ACGIH 1991]. A 23-year-old warehouse worker developed a skin reaction to calcium silicate after 3 days of exposure to an atmosphere described only as permeated with the silicate. The skin condition was characterized by patches of itchy, erythematous papular eruptions that cleared after work [Lachapelle 1984]. A study of 104 U.S. wollastonite workers with more than 1 year of exposure (mean duration of exposure approximately 9.2 years) showed no relationship between the prevalence of chronic bronchitis, airflow obstruction, or abnormal diffusing capacity in workers with increasing exposure to wollastonite [Rom 1983].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to calcium silicate include pain and redness of the eyes; itching, redness, and eruptions of the skin; and scratchiness of the throat.

2. *Chronic exposure:* Synthetic or natural materials that have calcium silicate as a base may cause dermal irritation after prolonged contact and possible induction of altered pulmonary function and lesions when silica or asbestos are also present.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils. If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium silicate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve calcium silicate and may result in worker exposures to this substance:

—Use as a substitute for materials containing silica in ceramics and as a substitute for asbestos in wallboard, insulation, and brake linings

—Use as a constituent of lime glass and Portland cement

—Use as a reinforcing filler in elastomers and plastics, paints, ceramics, paper, and wallboard

—Use as an anticaking ingredient in table salt, baking powder, foods, powdered pharmaceuticals, and cosmetics

—Use as an aggregate in road construction

—Use as a binder in refractory material, as a thermal insulator, and as a paper coating in chromatography

—Use as a veterinary antacid and absorbent

—Use as a carrier in the formulation of triazine herbicides and to provide free-flowing dust for toxic powders such as ground sulfur

The following methods are effective in controlling worker exposures to calcium silicate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium silicate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium silicate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium silicate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium silicate on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium silicate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne concentrations of calcium silicate (total dust) is determined by using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filters. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System under Dust (total) [OSHA 1989]. NIOSH has a similar method (Method 0500) that also involves gravimetric analysis [NIOSH 1984a]. The sample flow rate in the NIOSH method is between 1.5 and 2.0 liters/min. The minimum volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum sample volume at 15 mg/m^3 is 133 liters. The overall precision of the NIOSH method is 0.056.

A worker's exposure to airborne concentrations of calcium silicate (respirable fraction) is determined by using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is held in a 10-mm nylon cyclone, at a flow rate of 1.7 liter per minute until a maximum air volume of 800 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filters. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System under Dust (Respirable Nuisance) [OSHA 1989]. NIOSH has a similar method (Method 0600) that also involves gravimetric analysis [NIOSH 1984b]. The sample flow rate in the NIOSH method is 1.7 liter/min. The minimum volume for an airborne concentration of 5 mg/m^3 is 75 liters and the maximum sample volume at 5 mg/m^3 is 1,000 liters. The overall precision of the NIOSH method ranges from 0.043 on laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium silicate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium silicate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium silicate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cometics in areas where calcium silicate is handled, processed, or stored.

STORAGE

Calcium silicate should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of calcium silicate should be protected from physical damage. Because containers that formerly contained calcium silicate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium silicate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Use a wet method, a scoop, or a vacuum to clean up this material.
2. Place the material into a clean, dry container.
3. Cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and haz-

ardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium silicate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium silicate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium silicate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium silicate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium silicate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with calcium silicate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions for use. No reports have been published on the resistance of various protective clothing materials to calcium

silicate permeation. If permeability data are not available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium silicate.

If calcium silicate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium silicate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium silicate. Contact lenses should not be worn if the potential exists for calcium silicate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM SULFATE

INTRODUCTION

This guideline summarizes pertinent information about calcium sulfate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaSO_4$

- **Synonyms**

  Anhydrous calcium sulfate; anhydrous gypsum; anhydrous sulfate of lime; crysalba; dead-burned gypsum; drierite; gibs; karstenite; muriacite; natural anhydrite; sulfuric acid, calcium salt; thiolite

- **Identifiers**

  1. CAS No.: 7778-18-9
  2. RTECS No.: WS6920000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium sulfate is an odorless, noncombustible solid. The natural form of anhydrous calcium sulfate is known as the mineral anhydrite consisting of crystals or granules of varying color (e.g., white with a blue, gray, or reddish tinge or brick red). Insoluble anhydrite, which has the same crystal structure as the mineral, is obtained upon complete dehydration of gypsum at above 650°C. Soluble anhydrite is obtained in granular or powder form by complete dehydration of gypsum at or below 300°C in an electric oven.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 136.14
  2. Boiling point (760 mm Hg): 1,193°C (2,179.4°F)
  3. Specific gravity (water = 1): 2.96 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 1,450°C (2,642°F)
  6. Vapor pressure at 20°C (68°F): Not applicable
  7. Solubility: Anhydrous calcium sulfate is insoluble in water but soluble in acid, ammonium salts, sodium thiosulfate, and glycerin.
  8. Evaporation rate: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Reactivity**

1. Conditions contributing to instability: None reported

2. Incompatibilities: Explosions may result from contact of calcium sulfate with diazomethane, aluminum, or phosphorus.

3. Hazardous decomposition products: Toxic gases and particulates (such as oxides of sulfur) may be released in a fire involving calcium sulfate.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to calcium sulfate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Calcium sulfate will not burn. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium sulfate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium sulfate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium sulfate is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium sulfate (total dust) a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to calcium sulfate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium sulfate can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* There is no acute information on the effects of calcium sulfate exposure in experimental animals. A month-long exposure study in animals (undefined species, route, and doses) induced bronchitis and interstitial pneumonia while exposure for 9 months caused pulmonary changes resembling those found for pneumosclerosis [Voropaev 1967]. Female rats that received four 25-mg intraperitoneal injections of calcium sulfate (gypsum) showed a slight increase in cancer rates when compared to the controls 5.7% and 0%, respectively. Mean survival rates were similar 587 days for gypsum and 592 days for controls [Pott et al. 1976].

2. *Effects on Humans:* Calcium sulfate causes irritation of the eyes, skin, mucous membranes, and upper respiratory tract in humans. Conjunctivitis, rhinitis, laryngitis, sore throat, tracheal and bronchial irritation, nosebleeds, and impaired sense of smell and taste have been reported in workers exposed to this substance [Parmeggiani 1983; Genium 1990; NLM 1991]. Although chronic lung disease has not been reported among domestic calcium sulfate workers [ACGIH 1991], a Russian paper reported that unfavorable ambient dust loads among female workers in

the gypsum industry caused increased incidences of alveolar modular fibrosis, subatrophic rhinitis, laryngitis, and pharyngitis [Voropaev 1967]. It is unclear whether the gypsum processed in Russia also contained other lung toxicants such as quartz [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to calcium sulfate can cause redness and itching of the eyes, runny nose, sore throat, and irritation of the respiratory tract and skin.

2. *Chronic exposure:* Calcium sulfate is a mucous membrane irritant that can also affect the eyes, impair the sense of smell and taste, and can cause nosebleeds. It may also cause pulmonary nodular fibrosis.

- **Emergency procedures**

> WARNING!
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium sulfate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium sulfate and may result in worker exposures to this substance:

—Manufacture of phosphoric acid from phosphate rock

—Use as a drying agent for solids, organic liquids, and gases

—Use as a chemical intermediate in the manufacture of sulfuric acid and as a reagent in the laboratory detection of aflatoxins

—Use in the manufacture of tofu and as a dietary source of calcium in poultry

—Use as a food additive in canned vegetables, bakery products, cheeses, and as a bleaching agent in flour

—Use as an ingredient in a copper poisoning antidote in sheep

—Use as a paper filler and a component of cement

The following methods are effective in controlling worker exposures to calcium sulfate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

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A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium sulfate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

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The medical, environmental, and occupational history

interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

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OSHA's method for the determination of worker exposure to airborne concentrations of calcium sulfate (respirable fraction) is made by using a tared, low-ash polyvinyl chloride filter with a 5 micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is preceded by a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Dust (Respirable Nuisance) [OSHA 1987]. NIOSH has a similar method (Method 0600), which also involves gravimetric analysis [NIOSH 1984b]. The sample flow rate in the NIOSH method is 1.7 liter/min. The minimum sample volume for an airborne concentration of 5 mg/m^3 is 75 liters, and the maximum sample volume is 1,000 liters. The overall precision for the NIOSH method ranges from 0.043 to 0.145 in laboratory tests and from 0.144 to 0.227 in field tests.

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If calcium sulfate contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with calcium sulfate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium sulfate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium sulfate is handled, processed, or stored.

STORAGE

Calcium sulfate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium sulfate should be protected from physical damage and should be stored separately from aluminum, diazomethane, phosphorus, heat, sparks, and open flame. Because containers that formerly contained calcium sulfate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium sulfate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Avoid dust generation and remove all sources of heat and ignition.

2. Ventilate the area of the spill.

3. Use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium sulfate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

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  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium sulfate; there is no reportable quantity for this substance.

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  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium sulfate emitted or released from their facility annually.

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  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged skin contact with calcium sulfate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium sulfate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium sulfate.

If calcium sulfate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium sulfate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium sulfate. Contact lenses should not be worn if the potential exists for calcium sulfate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPROLACTAM DUST

INTRODUCTION

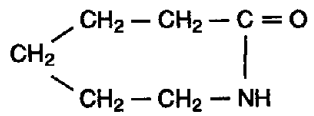
This guideline summarizes pertinent information about caprolactam dust for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NO$

- **Structure**



- **Synonyms**

Aminocaproic lactam; epsilon-caprolactam; 2-oxohexamethylenimine; 2-ketohexamethylenimine; 2-perhydroazepinone; Akulon; Alkamid; Amilan; ATM 2(Nylon); Bonamid; Capran 80; Caprolon B; Capron; Chemlon; Danamid; Durethan BK; Grilon; Itamid; Kaprolit; Maranyl; Miramid; Orgamide; Nylon X 1051; Plaskin 8200; Spencer 401; Tarlon XB; Ultramid; Vidlon

- **Identifiers (For caprolactam)**

1. CAS No.: 105-60-2
2. RTECS No.: CM3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Caprolactam dust is a white, crystalline, finely divided particulate that has an unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES (For caprolactam)

- **Physical data**

1. Molecular weight: 113.2
2. Boiling point (760 mm Hg): 266.9°C (512.42°F)
3. Specific gravity (water = 1): 1.02 at 75°C (167°F)
4. Vapor density (air = 1 at boiling point of caprolactam dust): 3.9
5. Melting point: 70°C (158°F)
6. Vapor pressure at 20°C (68°F): 0.001 mm Hg
7. Solubility: Soluble in water, benzene, chloroform, chlorinated hydrocarbons, cyclohexene, and petroleum fractions; freely soluble in methanol, ethanol, tetrahydrofurfuryl alcohol, ether, and dimethylformamide

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
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8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Moisture, heat, sparks, and open flame

2. Incompatibilities: Contact of caprolactam dust with strong oxidizing agents should be avoided.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving caprolactam dust.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to caprolactam; other sources rate caprolactam's fire hazard as slight.

1. Flash point: 125°C (257°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 1.84; upper, 8.0

4. Extinguishant: Use carbon dioxide, dry chemical, alcohol foam, or water fog to fight fires involving caprolactam dust. Water or foam may cause frothing. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be used to cool fire-exposed containers.

Fires involving caprolactum dust should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving caprolactam dust.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for caprolactam dust [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 3 mg/m^3 as a STEL. A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned caprolactam dust a threshold limit value (TLV) of 1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 3 mg/m^3 for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of convulsions, dermal sensitization, and dermal and respiratory irritation [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to caprolactam dust can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, caprolactam dust is an irritant of the eyes, nose, and skin and a central nervous system depressant. Applied to the eyes of rabbits, 20 mg of this substance caused a moderate degree of irritation; 500 mg of caprolactam applied to the skin of rabbits for 24 hr caused mild skin irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 1.4 g/kg [NIOSH 1993]. Acutely poisoned animals convulsed and showed other nervous system effects before death [NIOSH 1993]. The oral LD_{50} in rats is 1.2 g/kg; the LC_{50} in the same species is 300 mg/m^3 for 2 hr [NIOSH 1993]. Administered intraperitoneally, caprolactam at doses of 350 to 600 mg/kg caused tremor, convulsions, and a bloody eye discharge [Hathaway et al. 1991]. Guinea pigs tolerated seven daily 7-hr exposures to a concentration of caprolactam ranging from 118 to 261 mg/m^3 without

evidence of adverse effects other than occasional coughing [ACGIH 1991]. Male rats exposed 4 hr/day to a 125 mg/m^3 concentration of caprolactam dust for 2.5 months showed increasing excitability, changes in spermatogenesis, and a decrease in respiratory rate and urinary function [IARC 1986]. Exposure to a 11 mg/m^3 concentration on the same regimen caused no adverse reproductive effects [IARC 1986]. In a 3-generation reproductive study in rats fed caprolactam at a dietary dose of 5,000 or 10,000 ppm, this substance caused dose-related decreases in food consumption and in body weight in dams and pups; at a dietary level of 10,000 ppm, signs of minimal kidney toxicity were seen in males at autopsy, but no reproductive or fetotoxic effects were observed [ACGIH 1991]. A 2-year carcinogenicity bioassay of caprolactam in mice and rats showed negative results [IARC 1986].

2. *Effects on Humans:* In humans, exposure to caprolactam causes eye, skin, and respiratory tract irritation, convulsions, and, in some individuals, dermal sensitization [ACGIH 1991]. Repeated exposure of the skin to the dust of caprolactam causes peeling and fissuring in chronically exposed workers [ACGIH 1991]. Workers exposed to the fumes of caprolactam (condensed from the vapor) at concentrations ranging from 6 to 131 mg/m^3 for 9 months to 13 years reported sensory irritation and dermatitis; however, no caprolactam-related pulmonary effects or signs of systemic toxicity were seen in these workers [ACGIH 1991]. Another study showed that workers repeatedly exposed to caprolactam dust (condensed vapor) generated by the spinning process complained of a bitter taste, nervousness, nose bleeds, productive cough, and dry, split mucous membranes. Some complained of flatulence, heartburn, and a heavy feeling in the stomach [ACGIH 1991]. A group of male workers exposed to several chemicals, including caprolactam dust, showed an increase in sperm abnormalities, and women occupationally exposed to this substance have been reported to have an increased rate of complications during pregnancy; however, confounding exposures and other methodological problems make interpretation of these results difficult [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to caprolactam dust may cause redness, inflammation, and tearing of the eyes; redness and inflammation of the eyelids; runny nose; scratchy throat; coughing; and redness or blistering of the skin.

2. *Chronic exposure:* Chronic exposure to caprolactam dust may cause dermatitis (fissuring, peeling, and inflammation); some individuals become sensitized to caprolactam and may have an allergic skin reaction (i.e., hives) to this substance on subsequent exposure.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if caprolactam dust or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and procedures for protecting themselves in rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve caprolactam dust and may result in worker exposures to this substance:

—Use as a chemical intermediate in the production of nylon-6 fibers and plastics

—Use as a solvent for some high molecular weight polymers

—Use in making coatings, plasticizers, paint vehicles, and synthetic leather

The following methods are effective in controlling worker exposures to caprolactam dust, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to caprolactam dust, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to caprolactam dust at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, and respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to caprolactam dust exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of caprolactam dust on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for caprolactam dust.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne caprolactam dust is determined by using an OSHA Versatile Sampler (OVS-7), 13-mm XAD-7 tube (270/140-mg sections, 20/60 mesh), with a glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 100 liters (TWA) or 15 liters (STEL) is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If caprolactam dust contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with caprolactam dust should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of caprolactam dust.

A worker who handles caprolactam dust should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where caprolactam dust is present.

STORAGE

Caprolactam should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical equipment in use in storage areas should be of explosionproof design. Carrying equipment and storage containers should be grounded and bonded to prevent a dust explosion, and bulk storage systems should have an explosion-relief design. Containers of caprolactam dust should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained caprolactam dust may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving caprolactam dust, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.

5. Cover spill with sand, vermiculite, or soda ash and place material into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Caprolactam is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center about an accidental release of caprolactam dust; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of caprolactam dust emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although caprolactam dust is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of caprolactam dust exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. If the use of respirators is necessary, the only respirators permitted are those that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.1200]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with caprolactam dust. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to caprolactam dust permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to caprolactam dust.

If caprolactam dust is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which caprolactam dust might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with caprolactam dust. Contact lenses should not be worn if the potential exists for caprolactam dust exposure.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ATS [1987]. Standardization of spirometry—1987 update. American Thoracic Society. Am Rev Respir Dis 136:1285-1296.

CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

Hathaway GJ, Proctor NH, Hughes JP, Fischman ML [1991]. Chemical hazards of the workplace. Philadelphia, PA: J.B. Lippincott Company.

IARC [1986]. IARC monographs on the evaluation of carcinogenic risk of chemicals to humans. Vol. 39. Lyon, France: World Health Organization, International Agency for Research on Cancer.

NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPROLACTAM VAPOR

INTRODUCTION

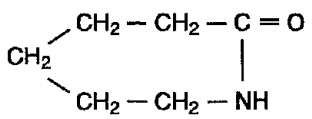
This guideline summarizes pertinent information about caprolactam vapor for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NO$

- **Structure**



- **Synonyms**

Aminocaproic lactam; epsilon-caprolactam; 2-oxohexamethylenimine; 2-ketohexamethylenimine; 2-perhydroazepinone; Akulon; Alkamid; Amilan; ATM-2 (Nylon); Bonamid; Capran 80; Caprolon B; Capron; Chemlon; Danamid; Durethan BK; Grilon; Itamid; Kaprolit; Maranyl; Miramid; Orgamide; Nylon X 1051; Plaskin 8200; Spencer 401; Tarlon XB; Ultramid; Vidlon

- **Identifiers (For caprolactam)**

1. CAS No.: 105-60-2
2. RTECS No.: CM3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Caprolactam vapor is caprolactam in the vapor state. The vapor evolves only at high temperatures, because the vapor pressure of caprolactam is low. Caprolactam vapor is colorless and has an unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES

(For caprolactam)

- **Physical data**

1. Molecular weight: 113.2
2. Boiling point (760 mm Hg): 266.9°C (512.42°F)
3. Specific gravity (water = 1): 1.02 at 75°C (167°F)
4. Vapor density (air = 1 at boiling point of caprolactam vapor): 3.9
5. Melting point: 70°C (158°F)
6. Vapor pressure at 20°C (682°F): 0.001 mm Hg

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7. Solubility: Soluble in water, benzene, chloroform, chlorinated hydrocarbons, cyclohexene, and petroleum fractions; freely soluble in methanol, ethanol, tetrahydrofurfuryl alcohol, ether, and dimethylformamide

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Moisture, heat, sparks, and open flame

2. Incompatibilities: Contact of caprolactam vapor with strong oxidizing agents should be avoided.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving caprolactam vapor.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to caprolactam vapor; other sources rate caprolactam's fire hazard as slight.

1. Flash point: 125°C (257°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 1.84; upper, 8.0

4. Extinguishant: Use carbon dioxide, dry chemical, alcohol foam, or water fog to fight fires involving caprolactam vapors. Water or foam may cause frothing. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be used to cool fire-exposed containers.

Fires involving caprolactam vapors should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving caprolactam vapor.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for caprolactam vapor [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.22 ppm (1 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.66 ppm (3 mg/m^3) as a STEL. A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned caprolactam vapor a threshold limit value (TLV) of 5 ppm (23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 10 ppm (46 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of convulsions, dermal and respiratory irritation, and dermal sensitization [NIOSH 1992]; the ACGIH limits are based on the risk of eye, skin, and upper respiratory tract irritation associated with exposure to caprolactam vapor [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to caprolactam vapor can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, caprolactam vapor is an irritant of the eyes, upper respiratory tract, and skin and a central nervous system depressant. Applied to the skin of rabbits for 24 hr, 500 mg of caprolactam caused mild skin irritation; instilled into the eyes of rabbits, 20 mg of this substance caused a moderate degree of irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 1.4 g/kg [NIOSH 1993]. Acutely poisoned animals convulsed and showed other nervous system effects before death [NIOSH

1993]. The oral LD_{50} for caprolactam in rats is 1.2 g/kg; the LC_{50} in the same species is 300 mg/m^3 for 2 hr [NIOSH 1993]. Administered intraperitoneally, caprolactam at doses of 350 to 600 mg/kg caused tremor, convulsions, and a bloody eye discharge [Hathaway et al. 1991]. Guinea pigs tolerated seven daily 7-hr exposures to a concentration of caprolactam ranging from 118 to 261 mg/m^3 without evidence of adverse effects, other than occasional coughing [ACGIH 1991]. A 2-year carcinogenicity study of caprolactam in rats and mice showed negative results [IARC 1986].

2. *Effects on Humans:* Caprolactam is a convulsant and an irritant of the eyes, nose, and throat in humans [ACGIH 1991]. Exposure to this substance has also caused skin sensitization in some individuals [ACGIH 1991]. Repeated contact of the skin with the solid causes only transient irritation, in contrast to prolonged contact with the dust, which causes dermatitis [ACGIH 1991]. At vapor concentrations that occasionally peaked at 100 ppm (460 mg/m^3), polymer plant workers reported experiencing severe and dose-related eye, nose, and throat irritation; eye irritation was not experienced below a concentration of 25 ppm, but transient nose and throat irritation occurred in some workers even at vapor concentrations of 10 ppm (46 mg/m^3) [ACGIH 1991]. Volunteers exposed to caprolactam vapor for unspecified periods at concentrations ranging from 53 to 521 mg/m^3 reported eye and upper respiratory tract irritation [ACGIH 1991]. A group of male workers exposed to caprolactam and other chemicals showed an increase in sperm abnormalities, and women occupationally exposed to this substance are reported to have experienced an increased rate of complications during pregnancy; however, confounding exposures and other methodological problems make interpretation of these results difficult [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to caprolactam vapor may cause redness, inflammation, and burning of the eyes; runny nose; scratchy throat; productive cough; transient skin redness; nose bleeds; a bitter taste in the mouth; and a feeling of nervousness.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to caprolactam vapor have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during an emergency.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve caprolactam vapor and may result in worker exposures to this substance:

—Use as a chemical intermediate in the production of nylon-6 fibers and plastics

—Use as a solvent for some high molecular weight polymers

—Use in making coatings, plasticizers, paint vehicles, and synthetic leather

The following methods are effective in controlling worker exposures to caprolactam vapor, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to caprolactam vapor, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to caprolactam vapor at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to caprolactam vapor exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of caprolactam vapor on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individ-

ual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for caprolactam vapor.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne caprolactam vapor is determined by using an OSHA Versatile Sampler (OVS7), 13-mm XAD-7 tube (270/140-mg sections, 20/60 mesh), with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 100 liters (TWA) or 15 liters (STEL) is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If caprolactam vapor contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with caprolactam vapor should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laudering contaminated clothing should be informed of the hazardous properties of caprolactam vapor.

A worker who is exposed to caprolactam vapor should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where caprolactam vapor is present.

STORAGE

Caprolactam should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical equipment in use in storage areas should be of explosionproof design. Containers of caprolactam vapor should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained caprolactam vapor may still hold product residues, they should be handled appropriately.

LEAKS

In the event of a leak involving caprolactam vapor, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Do not touch the leaked material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Cover the leaked material with sand, vermiculite, or soda ash and place material into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Caprolactam vapor is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release

notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of caprolactam vapor; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of caprolactam vapor emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although caprolactam vapor is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of caprolactam vapor exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with caprolactam vapor. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to caprolactam vapor permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to caprolactam vapor.

Safety glasses, goggles, or face shields should be worn during operations in which caprolactam vapor might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with caprolactam vapor. Contact lenses should not be worn if the potential exists for caprolactam vapor exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPTAFOL

INTRODUCTION

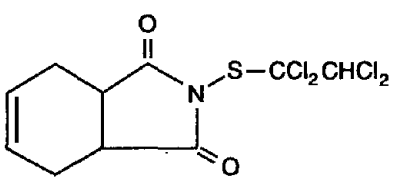
This guideline summarizes pertinent information about captafol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_9Cl_4NO_2S$

- **Structure**



- **Synonyms**

Difolatan; Captofol; Sanspor; Sulfonimide; 3a,4,7,7a-tetrahydro-2-((1,1,2,2-tetrachloroethyl)thio)-1-H-isoindole-1,3(2H)-dione; Alfloc 7020; Difosan; Folcid; Haipen 50; N-((1,1,2,2-tetrachloroethyl)sulfenyl)-cis-4-cyclohexene-1,2-dicarboximide; Nalco 7046; Ortho 5865; Proxel EF; cis-N-((1,1,2,2-tetrachloroethyl)thio)-4-cyclo-hexene-1,2-dicarboximide

- **Identifiers**

1. CAS No.: 2425-06-1
2. RTECS No.: GW4900000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Captafol is a noncombustible, white, crystalline substance with a characteristic odor. It is available commercially in the form of a liquid or wettable powder.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 349.06
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): Data not available
4. Vapor density: Not applicable
5. Melting point: 160° to 161°C (320° to 321.8°F) (decomposes)
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Insoluble in water; slightly soluble in acetone and most organic solvents; freely soluble in toluene.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Strongly alkaline conditions

2. Incompatibilities: Contact of captafol with acids or acid vapors may cause violent reactions.

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen and sulfur) may be released in a fire involving captafol.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to captafol; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving captafol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving captafol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for captafol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure. However, captafol has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned captafol a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek with a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the sensitization effects associated with exposure to captafol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to captafol can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Captafol is a liver and kidney toxicant; it also has fetotoxic and teratogenic effects in experimental animals. When instilled into rabbits' eyes it caused irritation of the conjunctiva and iris that lasted 21 days [ACGIH 1991]. Moderate skin irritation resulted when rabbits were dermally exposed to captafol for 72 hr [ACGIH 1991]. The dermal LD_{50} in the rabbit is 9 g/kg while it is <15 g/kg for the 80% wettable powder [NLM 1991; ACGIH 1991]. Rat oral LD_{50}s range from 2.5 to 6.8 g/kg [ACGIH 1991]. Dogs given 100 or 300 mg/kg captafol (route not specified) in a 2-yr study developed mild anemia and showed growth deficiency; the livers and kidneys of these animals and those given 30 mg/kg were slightly enlarged but showed no functional abnormalities [Hayes 1982]. Captafol is fetotoxic and/or teratogenic in rats, rabbits, and hamsters by the oral or peritoneal routes of exposure [NIOSH 1991; NLM 1991]. Captafol is also an experimental mutagen: it was positive in one in vivo and several in vitro tests [NLM 1991]. In a 2-yr cancer bioassay, rats were fed captafol at dietary levels of 250, 500,

1,500, or 5,000 ppm. Animals in the two highest dose groups did not grow normally and had enlarged livers; mortality was increased in animals dosed at the highest level. On microscopic examination, the livers and kidneys of animals given 1,500 or 5,000 ppm captafol showed kidney and pronounced degenerative liver changes, although there was no evidence of tumors [Hayes 1982; Clayton and Clayton 1981]. A second chronic study has confirmed captafol to be a carcinogen in treated mice [ACGIH 1991].

2. *Effects on Humans:* In humans, captafol is an irritant and sensitizer of the skin and upper respiratory system. Reactions to acute overexposure to captafol may be severe; sensitized workers develop wheezing and bronchitis [Clayton and Clayton 1981]. A 1969 survey of Japanese farmers reported a 25% incidence of occupational dermatitis in these workers; those farmers who had developed acute contact dermatitis had been engaged in the application of captafol and had developed red and swollen eyelids and dermatitis that was aggravated by light (phototoxic dermatitis). The skin eruptions typically appeared 1 to 3 days after contact and usually disappeared within a week after the cessation of exposure [Hayes 1982]. In one study, 23% of agricultural workers exposed to captafol reported episodes that suggested occupationally induced dermatitis [NLM 1991]. Another study reports that many of the captafol-exposed workers who had developed skin rash also showed signs of systemic toxicity: hypertension, anemia, decreased liver function, decreased excretion of urinary protein and urobilinogen, and depressed cholinesterase activity [Hayes 1982; ACGIH 1991]. Ingestion of large quantities have caused vomiting and diarrhea [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Captafol can induce wheezing, bronchitis, coughing, redness and tearing of the eyes, red and swollen eyelids, and reddened and blistered skin.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to captafol may include raised, itching, reddened, and blistered eruptions of the skin, asthmatic wheezing, hypertension, anemia, and decreased red blood cell cholinesterase activity and elevated liver function.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if captafol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** use syrup of ipecac if large amounts of captafol are ingested.

—Do ***not*** induce vomiting if captafol has been mixed with a petroleum distillate such as kerosene or diesel fuel.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve captafol and may result in worker exposures to this substance:

—Manufacture of captafol or captafol mixtures

—Formulation of captafol-containing fungicides

—Application of captafol-containing fungicides to tomatoes, potatoes, coffee plants, logs, and wood products

The following methods are effective in controlling worker exposures to captafol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to captafol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to captafol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of

exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory system and skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to captafol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of captafol on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for captafol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne captafol is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm tube (270/140 mg sections, 20/60 mesh) that has a glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 240 liters is collected. Analysis is conducted by gas chromatography using an electron capture detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989]

PERSONAL HYGIENE

If captafol contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with captafol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of captafol, particularly its potential to cause skin sensitization.

A worker who handles captafol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where captafol or a solution containing captafol is handled, processed, or stored.

STORAGE

Captafol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of captafol should be protected from physical damage and should be stored separately from acids, acid fumes, strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained captafol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving captafol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small dry spills, collect material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in an approved facility.

6. If captafol is in liquid or slurry form, absorb it with vermiculite, dry sand, earth, or a similar method.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Captafol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of captafol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of captafol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although captafol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of captafol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with captafol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to captafol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to captafol.

If captafol is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which captafol might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with captafol.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPTAN

INTRODUCTION

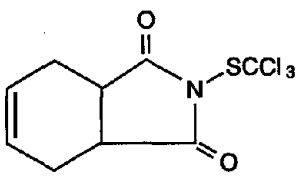
This guideline summarizes pertinent information about captan for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_8Cl_3NO_2S$

- **Structure**



- **Synonyms**

N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide; 3a,4,7,7a-tetrahydro-2-[(trichloromethyl)thio]-1H-isoindole-1,3(2H)-dione; AA Captan; Agrosol S; Agrox 2-Way and 3-Way; Amercide; Bangton; Bean Seed Protectant; Captaf; Captex; Esso Fungicide 406; Flit 406; Glyodex 37-22; Hexacap; Isotox Seed Treater "D" and "F"; Kaptan; Malipur; Merpan; Neracid; Orthocide; Vancide P-75; Vanicide

- **Identifiers**

1. CAS No.: 133-06-2
2. RTECS No.: GW5075000
3. DOT UN: 9099 31
4. DOT label: None

- **Appearance and odor**

Captan is an odorless, white, crystalline solid that can also be found as a yellow powder. This substance is available as a powder or in a variety of liquid formulations.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 300.57
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.74 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 178°C (352.4°F) (decomposes)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6 Vapor pressure at 25°C (77°F): Less than 0.00001 mm Hg

7. Solubility: Practically insoluble in water; soluble in acetone, benzene, chloroform, cyclohexanone, isopropanol, and xylene; insoluble in petroleum oils.

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat and alkalinity

2. Incompatibilities: Tetraethyl pyrophosphate and emulsifiable concentrate formulations of parathion

3. Hazardous decomposition products: Toxic gases (such as chlorine, phosgene, and oxides of nitrogen and sulfur) may be released in a fire involving captan.

4. Special precautions: Captan cannot be used with strong alkalies or with oil sprays.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to captan; this substance may burn, but it does not ignite readily.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or alcohol foam.

Fires involving captan should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of captan may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving captan. Structural firefighters' protective clothing may provide limited protection against fires involving captan.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for captan [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. However, captan has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned captan a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer that is associated with exposure to captan [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to captan can occur through inhalation, ingestion, and eye and skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, captan is an irritant and sensitizer of the skin. When applied to the skin of experimental animals (species not identified) at a dose of 900 mg/kg, captan caused slight irritation [ACGIH 1991], while previously exposed guinea pigs developed a moderate degree of sensitization when rechallenged [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is greater than 9 g/kg [Clayton and Clayton 1981]. The 2-hr LC_{50}s for male and female mice are 4,500 and 5,000 mg captan/m^3, respectively [ACGIH 1991]. However, mechanical

milling of that technical material reduced the 2-hr LC_{50}s in mice to 1,700 and 3,700 mg/m^3, respectively. Estimated inhalation absorption levels for the milled material were calculated to be 142 mg/kg for the males and 310 mg/kg for the females. The 2-hr LC_{50} for rats is greater than 5,700 mg/m^3 for unmilled captan [Stevens et al. 1978]. The lowest reported oral LD50s in mice and rats are 7,500 and 8,400 mg/kg [ACGIH 1991; IARC 1983]. Laboratory animals given very high doses (not further specified) of captan became hypothermic, irritable, anorectic, and listless; they also had hyporeflexia and oliguria [EPA 1989]. When tested in mice, rats, dogs, and monkeys at doses below those that are maternally toxic, captan failed to produce teratogenic effects by the oral, subcutaneous, or inhalation route of administration [Hayes 1982]. Although captan has not been shown to be teratogenic, feeding at maternally toxic doses has caused fetotoxicity (increased resorptions and decreased fetal weights) and possible terata (e.g., shortened forelimbs, cleft palate, fused ribs, exencephaly) among the offspring of some species [NLM 1991; IARC 1983]. Feeding studies demonstrated no effects in dogs fed 100 mg/kg/day for 66 weeks, but feeding at a dose of 300 mg/kg/day caused a slight increase in liver and kidney weights [Hayes 1982; ACGIH 1991]. Female rats fed 1,000 or 5,000 ppm captan in their diet (about 250 mg/kg/day) for 2 yr showed growth retardation; at twice this dose, captan caused growth depression in animals of both sexes and testicular atrophy in the males [Clayton and Clayton 1981; Hayes 1982]. Captan is mutagenic in direct contact with susceptible cells, but it is not mutagenic in intact animals, except perhaps at very high doses [Hayes 1982]. Captan was tested for carcinogenicity in mice and rats by dietary administration; it was carcinogenic in one strain of mice, in which it caused a statistically significant increase in the incidence of duodenal tumors [IARC 1983]. The International Agency for Research on Cancer (IARC) has concluded that there is limited evidence that captan is carcinogenic in experimental animals [IARC 1983]. Subsequent to the IARC review, rats and mice that were administered captan in their diets for 80 weeks developed neoplasms, including cancers. Rats developed neoplasms of the ovary, liver, and the pituitary, adrenal, and mammary glands. Mice had increased numbers of duodenal neoplasms [NLM 1991].

2. *Effects on Humans:* In humans, captan is an irritant of the eyes, skin, and upper respiratory tract and a skin sensitizer [Hayes 1982; Klaassen et al. 1986; Clayton and Clayton 1981]. Skin contact with captan has caused severe sensitivity in some workers, and an estimated 3% to 5% of the exposed population could become sensitized [IARC 1983]. An 18-year-old gardener was confirmed as having recurrent urticaria from exposure to captan [NLM 1991]. A 1,071 mg/kg dose of captan caused the death of one individual [NIOSH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Captan can induce redness, pain, and tearing of the eyes; runny nose; scratchy throat; difficult breathing; and redness, itching, and cracking of the skin.

2. *Chronic exposure:* Captan-sensitized workers can develop redness, raised areas, blistering, and itching of the skin.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if captan or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve captan and may result in worker exposures to this substance:

—Manufacture and formulation of captan-containing fungicides and bactericides

—Use as a fungicide to control scab, black root, botrytis, sooty blotch, and summer rots on apples and for control of a wide variety of fungal diseases on small fruits, berries, vegetables, and ornamental crops

—Use as a bacteriostat in soaps

—Use as a fungicide in paints, lacquers, paper, rubber stabilizers, vinyl resins, plastics, leather fabrics, and to preserve cosmetics and fruits

—Use as a bacteriostat and fungicide in veterinary medicine

The following methods are effective in controlling worker exposures to captan, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to captan, a licensed health care professional should evaluate and document the worker's baseline

health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to captan at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory tract or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to captan exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of captan on the respiratory tract or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for captan.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne captan is determined by using an OSHA Versatile Sample (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If captan contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with captan should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of captan, particularly its potential to cause skin sensitization.

A worker who handles captan should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where captan or a solution containing captan is handled, processed, or stored.

STORAGE

Captan should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of captan should be protected from physical damage and should be stored separately from water and heat. Because containers that formerly contained captan may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving captan, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the captan for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Captan is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for captan is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of captan per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of captan emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although captan is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this

substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of captan exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with captan. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to captan permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to captan.

If captan is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which captan might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with captan. Contact lenses should not be worn if the potential exists for captan exposure.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBOFURAN

INTRODUCTION

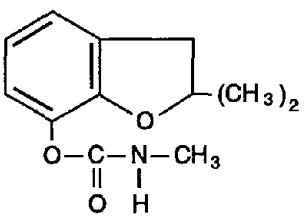
This guideline summarizes pertinent information about carbofuran for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{15}NO_3$

- **Structure**



- **Synonyms**

Bay 70143; Niagra 10242; Furadan; Furodan; Yaltox; Curaterr; Chinufur; 2,2-dimethyl-2,2-dihydrobenzofuranyl-7-N-methylcarbamate; methyl carbamic acid 2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester

- **Identifiers**

1. CAS No.: 1563-66-2
2. RTECS No.: FB9450000
3. DOT UN: 2757 55
4. DOT label: Poison B

- **Appearance and odor**

Carbofuran is a noncombustible, odorless, colorless or white crystalline solid available commercially in the form of wettable powder, granules, or flowable paste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 221.26
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.18 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of carbofuran): Data not available
5. Melting point: 150° to 152°C (302° to 305.6°F)
6. Vapor pressure at 33°C (91.4°F): 0.00002 mm Hg
7. Solubility: Slightly soluble in water; soluble in ace-

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tone, acetonitrile, benzene, cyclohexanone, and other organic solvents. In the conventional solvent formulations used in agriculture, carbofuran is essentially insoluble.

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, flame, or contact with an alkaline substance

2. Incompatibilities: Fires and explosions may result from contact of carbofuran with alkaline media, acids, or strong oxidizers (such as perchlorates, peroxides, chlorates, nitrates, and permanganates).

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving carbofuran.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to carbofuran; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving carbofuran.

Fires involving carbofuran should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbofuran may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbofuran. Chemical protective clothing that is specifically recommended for carbofuran may provide little or no thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving carbofuran.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for carbofuran [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbofuran a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to carbofuran.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbofuran can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbofuran is a potent but reversible cholinesterase inhibitor. Instillation of carbofuran into the conjunctival sac caused miosis and paralysis of the ciliary muscle, both reversed by installation of atropine [Tobin 1970]. There are widely divergent dermal LD_{50}s for rabbits which range from 885 mg/kg [NIOSH 1992b] to 10,200 mg (98% carbofuran)/kg [Tobin 1970]. The rat dermal LD_{50} is 120 mg/kg [NIOSH 1992b]. The LC_{50} in rats is 85

mg/m^3 for an unspecified period [NIOSH 1992b]. Monkeys which inhaled a 75% wettable powder (wp) dust for 6 hr at an airborne concentration of 0.86 mg/m^3 showed slight but significant cholinesterase inhibition; at an exposure of 0.56 mg/m^3 for the same period, no effects were seen. In addition, a monkey had sporadic tremors following a 30-min exposure to 1.3 mg/m^3. Another exposed to 1.8 mg/m^3 for 260 min developed only emesis [Tobin 1970]. The oral LD_{50}s for mice, rats, and dogs are 2, 5, and 19 mg/kg, respectively [NIOSH 1992b]. In experimental animals given high but non-lethal doses of carbofuran, normal cholinesterase activity returned within 6 hr [NLM 1991]. Dogs fed 50 ppm carbofuran in a chronic feeding study (length of study not specified) showed significant inhibition of plasma, erythrocyte, and brain cholinesterase levels; the no-effect levels in dogs and rats were 20 ppm (dogs) and 25 ppm (rats) [ACGIH 1991]. Administered to rats by gavage on day 18 of gestation, a dose of 2.5 mg/kg carbofuran produced cholinergic signs within 5 minutes and killed 25% of the dams within 30 minutes; a dose of 0.05 mg/kg produced nervous system effects in the dams but not in the fetuses [Hayes 1982]. No adverse reproductive or developmental effects were induced in three successive generations of rats which consumed diet containing carbofuran (10 mg/kg diet) or in dogs on a 50 mg carbofuran/kg diet for one generation [NIOSH 1992b]. When mice, rats, rabbits, and dogs consumed diets containing carbofuran (100 mg/kg), the only effect induced was decreased survival rates in rat pups [Shepard 1986]. Carbofuran is mutagenic in bacterial and mammalian test systems [NIOSH 1992b; NLM 1991].

2. *Effects on Humans:* In humans, carbofuran is a rapidly reversible cholinesterase inhibitor. No effects have been reported in workers exposed to carbofuran concentrations approaching 0.1 mg/m^3 per day [NLM 1991]. Several cases of carbofuran poisoning have been reported in laboratory and pilot plant personnel and applicators. These workers developed weakness, malaise, profuse perspiration, lightheadedness, paleness, nausea, blurred vision, loss of depth perception, hypersalivation, poor coordination, and vomiting. Recovery took up to 4 hr in the absence of atropine treatment and less than 30 min when it was administered. No systemic toxicity was observed when only ocular effects were induced [Tobin 1970]. Seventy-four of 142 teenage workers who worked in a field that had been sprayed with carbofuran the previous day experienced pronounced symptoms of nervous system poisoning, including dizziness, nausea, and/or blurred vision; however, all of these workers responded quickly and completely to therapy [Hayes 1982]. Carbofuran is mutagenic in human lymphocyte cells [NIOSH 1992b].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbofuran can cause muscle weakness, dizziness, profuse sweating, headache, salivation, nausea, vomiting, abdominal pain, diarrhea, contracted pupils, incoordination, slurred speech, difficult breathing, chest tightness, blurred vision, muscle twitching and spasms. Convulsions may occur.

2. *Chronic exposure:* Based on effects seen in animals, long-term exposure to low levels of carbofuran is likely to cause cholinesterase inhibition.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Carbofuran can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbofuran or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** induce vomiting if carbofuran has been mixed with a petroleum distillate such as kerosene or diesel fuel.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbofuran and may result in worker exposures to this substance:

—Use as an acaricide, miticide, nematocide, and insecticide

—Manufacture of carbofuran

—Formulation of carbofuran for use as a pesticide

The following methods are effective in controlling worker exposures to carbofuran, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbofuran, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate

on the function and integrity of the blood and on the individual's pre-exposure plasma and red blood cell cholinesterase activity levels.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbofuran at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma or red blood cell cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbofuran exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbofuran on plasma or red blood cell cholinesterase activity levels. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of overexposure to organophosphorus compounds such as carbofuran. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for carbofuran (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability. Absorption of carbofuran can be confirmed by analysis of urine for its metabolite, carbofuran phenol. However, correlations between airborne and urinary levels of carbofuran and its metabolite have not been established.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbofuran is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/60 mesh). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 480 liters is collected. The sample is then treated with acetonitrile to extract the carbofuran. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If carbofuran contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with carbofuran should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbofuran.

A worker who handles carbofuran should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbofuran or a solution containing carbofuran is handled, processed, or stored.

STORAGE

Carbofuran should be stored in a cool, dry, continuously-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbofuran should be protected from physical damage and should be stored separately from acids, strong oxidizers (such as perchlorates, peroxides, and nitrates), heat, sparks, and open flame. Because containers that formerly contained carbofuran may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbofuran, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

5. For liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility at which there are 10,000 lb or more of carbofuran must comply with EPA's emergency planning requirements. (If carbofuran is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 10 lb or more of carbofuran are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for carbofuran is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbofuran emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbofuran is not specifically listed as

a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbofuran exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with carbofuran. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to carbofuran permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to carbofuran.

If carbofuran is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbofuran might contact the eyes (e.g., through dust particles or splashes of carbofuran-containing solutions). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbofuran. Contact lenses should not be worn if the potential exists for carbofuran exposure.

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CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

Hayes WJ, Jr. [1982]. Pesticides studied in man. Baltimore, MD: Williams & Wilkins.

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protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON TETRABROMIDE

INTRODUCTION

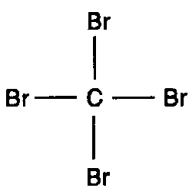
This guideline summarizes pertinent information about carbon tetrabromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CBr_4

- **Structure**



- **Synonyms**

  Carbon bromide, tetrabromomethane, methane tetrabromide

- **Identifiers**

  1. CAS No.: 558-13-4
  2. RTECS No.: FG4725000
  3. DOT UN: 2516 53
  4. DOT label: St. Andrew's Cross

- **Appearance and odor**

  Carbon tetrabromide is a nonflammable, colorless to yellow-brown, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 331.65
  2. Boiling point (760 mm Hg): 189.5°C (373.1°F)
  3. Specific gravity (water = 1): 3.42
  4. Vapor density (air = 1 at boiling point of carbon tetrabromide): 11.4
  5. Melting point: 90.1°C (194.2°F)
  6. Vapor pressure at 96.3°C (205°F): 40 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol, ether, chloroform, and other organic solvents
  8. Evaporation rate: Data not available

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- **Reactivity**

1. Conditions contributing to instability: None reported

2. Incompatibilities: Contact of carbon tetrabromide with lithium or hexylcyclohexyldilead may cause an explosion.

3. Hazardous decomposition products: Toxic gases (such as bromine) may be released in a fire involving carbon tetrabromide.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to carbon tetrabromide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or regular foam.

Fires involving carbon tetrabromide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbon tetrabromide. Structural firefighters' protective clothing may provide limited protection against fires involving carbon tetrabromide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for carbon tetrabromide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (1.4 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.3 ppm (4 mg/m^3) as a STEL. A STEL is a 15-min TWA exposure that should not be exceeded at any time during the workday [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbon tetrabromide a threshold limit value (TLV) of 0.1 ppm (1.4 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (4.1 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of eye, skin, lung, and liver irritation, and hepatotoxic effects associated with exposure to carbon tetrabromide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbon tetrabromide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbon tetrabromide is a severe irritant of the eyes and respiratory tract as well as a liver and kidney toxicant. Undiluted carbon tetrabromide applied to the eyes of rabbits caused severe irritation and permanent corneal damage. However, when the material was promptly washed from the eyes, pain and irritation were noted but the corneal damage was reversible. Exposure of rats to carbon tetrabromide fume at 10 mg/m^3 for 4 hr daily caused irritation of the eyes and respiratory tract [Clayton and Clayton 1981]. Contact with the skin of rabbits caused relatively slight irritation, but when the material was confined tightly to the skin, it caused hyperemia and a moderate degree of swelling [Clayton and Clayton 1981]. The subcutaneous LD_{50} in mice is 298 mg/kg [NIOSH 1992b] and the rat oral

LD_{50} is 1,800 mg/kg [Clayton and Clayton 1981]. Rats exposed to 10 to 1,000 mg/m^3 (0.07 to 74 ppm) for 4 hr/day during a 4-month period exhibited metabolic changes in the liver [Clayton and Clayton 1981]. Rats repeatedly exposed to 100 mg/m^3 or to 300 to 500 mg/m^3 (depending on the analytical method) for 7 hr/day, 5 days/week during a 6-month period showed no effects, but exposure to higher (not further specified) concentrations caused poor growth; fatty and degenerative changes of the liver appeared at autopsy [Clayton and Clayton 1981].

2. *Effects on Humans:* Carbon tetrabromide is a severe irritant of the eyes, nose, throat, and lungs; it is also a liver toxicant. The vapor of carbon tetrabromide causes pronounced eye irritation and lacrimation even at low concentrations [Clayton and Clayton 1981]. Exposure to high concentrations (not further specified) of carbon tetrabromide vapors can irritate the upper respiratory tract, cause CNS depression, and injure the lungs, liver, and kidneys [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to carbon tetrabromide can induce corneal damage, profuse tearing and burning of the eyes; ocular, skin, and upper respiratory tract irritation; and CNS depression.

2. *Chronic exposure:* Liver damage is the primary response to chronic exposure to carbon tetrabromide at very low concentrations [Clayton and Clayton 1981]. Chronic exposure to low concentrations of carbon tetrabromide can also induce contact irritation.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritaiton!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of carbon tetrabromide. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbon tetrabromide or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

Workers may be exposed to carbon tetrabromide during its use as an intermediate in the manufacture of other chemicals.

The following methods are effective in controlling worker exposures to carbon tetrabromide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbon tetrabromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and liver.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbon tetrabromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or liver.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbon tetrabromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbon tetrabromide on the eyes, skin, and liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for carbon tetrabromide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's

health status should be compared with those expected for a suitable reference population. Because occupational exposure to carbon tetrabromide may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbon tetrabromide is determined by using an XAD-4 tube (80/40-mg sections, 15/50 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters (TWA) or 3 liters (STEL) is collected. The sample is then treated with toluene to extract the carbon tetrabromide. Analysis is conducted by gas chromatography using an electron capture detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If carbon tetrabromide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with carbon tetrabromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of carbon tetrabromide, particularly its potential to cause burns of the eyes and skin.

A worker who handles carbon tetrabromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbon tetrabromide or a solution containing carbon tetrabromide is handled, processed, or stored.

STORAGE

Carbon tetrabromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbon tetrabromide should be protected from physical damage and should be stored separately from strong oxidizers, lithium, hexylcyclohexyldilead, heat, sparks, and open flame. Because containers that formerly contained carbon tetrabromide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving carbon tetrabromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Use a clean shovel and gently place the spilled material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbon tetrabromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the National Response Center of an accidental release of carbon tetrabromide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbon tetrabromide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbon tetrabromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbon tetrabromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, gauntlets, aprons, coveralls, and other clothing, as appropriate) should be worn to prevent any skin contact with carbon tetrabromide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. A Viton/neoprene laminate has been tested against carbon tetrabromide and has demonstrated good resistance. A laminate of butyl rubber and neoprene has demonstrated poor resistance to permeation by carbon tetrabromide.

If carbon tetrabromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbon tetrabromide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbon tetrabromide. Contact lenses should not be worn if the potential exists for carbon tetrabromide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON TETRACHLORIDE

INTRODUCTION

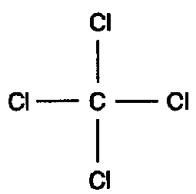
This guideline summarizes pertinent information about carbon tetrachloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

CCl_4

- **Structure**



- **Synonyms**

Tetrachloromethane; perchloromethane; methane tetrachloride; Nectorina; benzinoform; carbon chloride; Carbona; carbon tet

- **Identifiers**

1. CAS No.: 56-23-5
2. RTECS No.: FG4900000
3. DOT UN: 1846 55
4. DOT label: Poison

- **Appearance and odor**

Carbon tetrachloride is a noncombustible, colorless liquid with a sweet, aromatic, etherlike odor. The best estimate of the odor threshold for carbon tetrachloride is 250 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 153.84
2. Boiling point (760 mm Hg): 76.7°C (170°F)
3. Specific gravity (water = 1): 1.59 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of carbon tetrachloride): 5.3
5. Melting point: –23°C (–9.4°F)
6. Vapor pressure at 20°C (68°F): 91.3 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; miscible with alcohol, benzene, chloroform, ether, carbon disulfide, petroleum ether, and oils

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: None reported

2. Incompatibilities: Contact of carbon tetrachloride with fluorine gas, alkali metals, or aluminum may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as phosgene and hydrogen chloride) may be released in a fire involving carbon tetrachloride. When used to put out electrical fires, carbon tetrachloride may evolve phosgene gas.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to carbon tetrachloride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is appropriate for the materials involved in the surrounding fire.

Fires involving carbon tetrachloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbon tetrachloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Fire fighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbon tetrachloride. Chemical protective clothing that is specifically recommended for carbon tetrachloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural Fire fighters' protective clothing is not effective against fires involving carbon tetrachloride.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbon tetrachloride is 10 ppm as an 8-hr time-weighted average (TWA) concentration with a ceiling concentration of 25 ppm that may not be exceeded during an 8-hr workday except for a 5-min period every 4 hours; the acceptable maximum peak during this 5-min period is 200 ppm [29 CFR 1910.1000, Table Z-2].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) designates carbon tetrachloride a potential occupational carcinogen and has established a recommended exposure limit (REL) for this substance of 2 ppm (12.6 mg/m^3) as a 60-min short-term exposure limit (STEL) [NIOSH 1992a]. The STEL is a 60-min TWA exposure that shall not be exceeded at any time during a workday.

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated carbon tetrachloride an A2 substance (suspected human carcinogen) and has assigned carbon tetrachloride a threshold limit value (TLV) of 5 ppm (31 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned carbon tetrachloride a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cancer associated with exposure to carbon tetrachloride [ACGIH 1993; NIOSH 1992a].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbon tetrachloride can occur through inhalation of the vapor, eye or skin contact, absorption through the skin of the liquid, or ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbon tetrachloride is an eye and skin irritant, a liver and kidney toxin, and a carcinogen. This chemical is a mild eye and skin irritant in rabbits [NIOSH 1992b]. Monkeys demonstrated little dermal absorption from ambient exposures. Likewise, rats dermally exposed to the liquid required large doses to induce lethality [Clayton and Clayton 1981]. The dermal LD_{50} in rats is 5,070 mg/kg [NIOSH 1992b]. The maximum exposures that caused no effects in male rats were: 3,000 ppm for 6 min, 800 ppm for 30 min, and 50 ppm for 7 hr [Clayton and Clayton 1981]. The highest airborne concentrations in which rats survived were 12,000 ppm for 15 min and 3,000 ppm for 8 hr [Clayton and Clayton 1981]. The LC_{50} in rats and mice are 8,000 ppm for 4 hr and 9,526 ppm for 8 hr, respectively [NIOSH 1992b]. The oral LD_{50} in rats is 2,350 mg/kg [NIOSH 1992b]. Rats, guinea pigs, rabbits, and monkeys were exposed to carbon tetrachloride vapors for 7 hr/day, 5 days/week for up to 4 months. Rats, guinea pigs, and rabbits all showed histologic damage to the liver after exposures of 10 ppm or higher but not after exposure to 5 ppm; monkeys exhibited histologic damage to the liver at concentrations of 100 ppm or above but not at lower levels [Clayton and Clayton 1981]. Carbon tetrachloride was embryotoxic and fetotoxic but not teratogenic in rats exposed to 300 to 1,000 ppm for 7 hr/day on days 6 to 15 of gestation [IARC 1979; NIOSH 1992b]. This chemical also increased fetal mortality when pregnant mice were given a single 150 mg dose [IARC 1979]. Carbon tetrachloride is weakly mutagenic in a wide variety of test systems [NIOSH 1992b]. This chemical produced liver tumors as well as cancers in mice, rats, and hamsters following administration by several routes, including inhalation and ingestion [ACGIH 1991; IARC 1979]. The International Agency for Research on Cancer (IARC) has determined that there is sufficient evidence of carbon tetrachloride's carcinogenicity in animals and that it is a Group 2B carcinogen (possibly carcinogenic in humans) [IARC 1987].

2. *Effects on Humans:* In humans, carbon tetrachloride is a mild eye and skin irritant, a central nervous system depressant, and a liver and kidney toxin. NIOSH, ACGIH, and other organizations classify carbon tetrachloride as a potential human carcinogen. The vapor of carbon tetrachloride is mildly irritating to the eyes [Grant 1986]; and has also caused visual disturbances (concentric restriction of color fields) [NLM 1991]. Prolonged or repeated contact of the liquid with the skin can cause pain, erythema, hyperemia, weal formation, tissue defatting and blistering [Grant 1986; Hathaway et al. 1991; NLM 1991]. The estimated no-observed-effect level for acute human exposure is 10 ppm for 3 hr [Hathaway et al. 1991]. A TC_{Lo} (lowest concentration causing an effect) exposure of 20 ppm (duration undefined) or 317 ppm for 30 min has produced nausea and vomiting [NIOSH 1992b]. Acute symptoms can include abdominal cramps, nervousness, dyspnea, cyanosis, oliguria, proteinuria, hepatomegaly, and optic neuritis [NIOSH 1992b]. Polycythemia, anemia, and hemodilution also may follow acute exposure [Hathaway et al. 1991]. Mild acute poisoning can result in renal injury, and decreased renal blood flow and filtration, which may require up to 200 days for complete recovery. In severe acute poisoning, anuria and terminal uremia require active restoration of renal function, or death occurs [NLM 1991]. In humans, the majority of fatalities caused by inhalation of carbon tetrachloride have been the result of renal injury with secondary cardiac failure. Liver damage occurs more often from ingestion of the liquid than from inhalation of the vapor [Hathaway et al. 1991]. Persons consuming alcohol, those with poor nutritional status, and persons with pre-existing liver or kidney disease are more susceptible to poisoning by carbon tetrachloride [Gosselin et al. 1984]. Human fatalities caused by acute renal failure have resulted from exposure to carbon tetrachloride concentrations of 50,000 ppm for 5 min [NLM 1991], 1,000 to 2,000 ppm for 30 min to 1 hr [Hathaway et al. 1991], or oral doses that exceed 1,500 mg/kg [NIOSH 1992b]. Although repeated exposure of workers to 10 ppm did not induce signs or symptoms of toxicity, 25 to 30 ppm caused nausea, vomiting, dizziness, drowsiness, and headache [NLM 1991]. Ten out of 17 workers exposed for an unspecified period to a 45- to 97-ppm concentration of carbon tetrachloride reported experiencing headache and giddiness, and several of these workers also had symptoms of liver dysfunction [ACGIH 1991]. Workers exposed to carbon tetrachloride at unspeci-

fied levels have experienced dizziness, vertigo, mental confusion, and incoordination, all signs and symptoms of central nervous system depression, and some have developed loss of visual acuity, convulsions, and cardiac arrhythmias [Hathaway et al. 1991]. Carbon tetrachloride has been confirmed as a weak mutagen in a variety of assays [NIOSH 1992b]. In the preamble of the 1989 *Air Contaminants; Final Rule,* OSHA concluded that an "occupational exposure to carbon tetrachloride at the 10-ppm PEL presents a significant risk of cancer to workers" [54 Fed. Reg. 2681 (1989)]. IARC has concluded that there is insufficient human data to directly classify carbon tetrachloride's carcinogenic risk to humans [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbon tetrachloride can induce mild irritation of the eyes and skin, with redness and inflammation, and central nervous system depression, with symptoms of malaise, headache, dizziness, incoordination, confusion, stupor, coma, and convulsions; nausea, vomiting, abdominal pain, and diarrhea are also frequent. Acute exposures can lead to ventricular fibrillation (rapid, irregular heartbeat) and death from cardiac failure. Acute oral exposures have primarily caused liver damage, as evidenced by an enlarged and tender liver and jaundice, as well as acute nephritis, with a decrease in the volume of urinary output and the presence of blood, pus, or protein in the urine. Acute renal failure can result in coma and death.

2. *Chronic exposure:* Repeated contact of the skin with carbon tetrachloride may cause defatting of the skin and dermatitis, with redness and blister formation. Chronic exposure has also been associated with nausea, vomiting, dizziness, drowsiness, headache, visual disturbances, and loss of visual acuity. The IARC classifies carbon tetrachloride as possibly carcinogenic to humans based on sufficient animal data.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of carbon tetrachloride. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbon tetrachloride or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by touching the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbon tetrachloride and result in worker exposures to this substance:

—Manufacture of fluorocarbons for aerosols, refrigerants, and fire extinguishants (these uses of fluorocarbons have been largely phased out or banned)

—Use as a solvent in dry cleaning and in industry to dissolve resins, oils, fats, varnishes, and rubber waxes

—Use as an agricultural grain fumigant, pesticide, and anthelmintic and as an agent to extract oil from flowers and seeds

—Use in polymer technology as a reaction medium, catalyst, and chain transfer agent

—Use in organic synthesis for the chlorination of organic compounds and in the soap and perfume industries

—Use as a laboratory solvent

—Use in tin recovery and catalyst regeneration and as a cleaning agent for machinery and electrical equipment

The following methods are effective in controlling worker exposures to carbon tetrachloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbon tetrachloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and nervous system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbon tetrachloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of excessive alcohol intake and other findings consistent with diseases of the liver, kidney, or nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the

employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbon tetrachloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbon tetrachloride on the liver, kidneys, or nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although carbon tetrachloride can be detected in the breath of exposed workers, data on the correlation between breath concentrations and airborne concentrations of carbon tetrachloride are not available. Therefore, no biological monitoring test acceptable for routine use has yet been developed for carbon tetrachloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to carbon tetrachloride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbon tetrachloride is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a maximum air volume of 15 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg, and the method is described in NIOSH Method No. 1003 [NIOSH 1984].

PERSONAL HYGIENE

This substance can be absorbed through the skin in toxic amounts. Therefore, if carbon tetrachloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with carbon tetrachloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbon tetrachloride, particularly its potential to cause severe central nervous system effects on acute exposure.

A worker who handles carbon tetrachloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbon tetrachloride is handled, processed, or stored.

STORAGE

Carbon tetrachloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbon tetrachloride should be protected from physical damage and direct sunlight and should be stored separately from aluminum, barium, dimethyl formamide, magnesium, potassium, sodium, triethylaluminum, calcium disilicide decaborane, ethylene, heat, sparks, and open flame. Because containers that formerly contained carbon tetrachloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbon tetrachloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. Use water spray to reduce vapors.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the carbon tetrachloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbon tetrachloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbon tetrachloride is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of carbon tetrachloride per calendar year are required by EPA [49 CFR Part 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbon tetrachloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Carbon tetrachloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 355.40], and has been assigned EPA Hazardous Waste No. U211. This chemical is approved for land disposal as long as the concentration of carbon tetrachloride in the waste or treatment residual does not exceed 5.6 mg/kg. Carbon tetrachloride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbon tetrachloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with carbon tetrachloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by carbon tetrachloride and may provide protection for periods greater than 8 hr: polyvinyl alcohol, Viton, Barricade®, and Responder®. Materials that may withstand permeation for more than 4 but fewer than 8 hr are Teflon and a polyethylene/ethylene vinyl laminate. Protective clothing made of butyl rubber, natural rubber, neoprene, nitrile rubber, polyethylene, or polyvinyl chloride are not recommended for protection against permeation by carbon tetrachloride.

If carbon tetrachloride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbon tetrachloride might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbon tetrachloride. Contact lenses should not be worn if the potential exists for carbon tetrachloride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBONYL FLUORIDE

INTRODUCTION

This guideline summarizes pertinent information about carbonyl fluoride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CF_2O

- **Synonyms**

  Carbon difluoride oxide, carbon fluoride oxide, carbon oxyfluoride, carbonyl difluoride, difluoroformaldehyde, fluoroformyl fluoride, fluorophosgene, carbonic difluoride

- **Identifiers**

  1. CAS No.: 353-50-4
  2. RTECS No.: FG6125000
  3. DOT UN: 2417 15
  4. DOT label: Poison Gas

- **Appearance and odor**

  Carbonyl fluoride is a noncombustible, colorless, hygroscopic gas with a pungent and very irritating odor. It is shipped as a liquefied gas under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 66.01
  2. Boiling point (760 mm Hg): -83°C (-117.6°F)
  3. Specific gravity (water = 1): 1.14 at -114°C (-173°F)
  4. Vapor density: Data not available
  5. Melting point: -114°C (-173°F)
  6. Vapor pressure at 21.1°C (70°F): 42,104 mm Hg
  7. Solubility: Instantly hydrolyzed by water; decomposes in alcohol
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Heat and moisture
  2. Incompatibilities: Contact with moisture causes the instantaneous hydrolysis of carbonyl fluoride to very corrosive and toxic hydrogen fluoride gas and carbon dioxide.

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases (such as oxides of fluorine and carbon) may be released in a fire involving carbonyl fluoride.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to carbonyl fluoride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical or carbon dioxide for small fires; water spray, fog, or regular foam for large fires.

Fires involving carbonyl fluoride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbonyl fluoride may explode in the heat of the fire and should be removed if it is possible to do safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do not get water inside the containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbonyl fluoride. Structural firefighters' protective clothing is not effective against fires involving carbonyl fluoride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) had not promulgated a permissible exposure limit (PEL) for carbonyl fluoride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (5 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 5 ppm (15 mg/m^3) as a STEL. A STEL is a 15 min exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbonyl fluoride a threshold limit value (TLV) of 2 ppm (5.4 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 5 ppm (13 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of irritation associated with exposure to carbonyl fluoride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbonyl fluoride can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Carbonyl fluoride gas causes severe contact irritation or corrosion of tissues following acute exposure. In the presence of humidity or tissue fluids, it is rapidly hydrolyzed to two moles of hydrofluoric acid which is primarily responsible for the toxic effects elicited in exposed subjects. A near-lethal acute exposure, 310 ppm for 1 hr, of sacrificed mice, rats, guinea pigs, rabbits, and dogs resulted in the following histological lung changes: focal hemorrhage and edema at 24 hr; cellular repair with decreased edema at 48 hr; repair of damaged alveolar capillaries before 7 days; and a small amount of irreversible focal emphysema and mild interstitial fibrosis at the terminal 3-week sacrifice. The LC_{50}s in rats are 360 ppm for 1 hr and 90 ppm for 4 hr [NIOSH 1991]. Death resulted from respiratory or cardiac failure [NIOSH 1991; Scheel et al. 1968a]. Rats were exposed to polytetrafluoroethylene (PTFE) pyrolysis products containing hydrolyzable fluoride equal to a 50-ppm concentration of carbonyl fluoride for 1 hr/day for 5 days. Daily urinary fluoride levels reached 14 times normal on the first exposure day and continued to be markedly elevated 18 days after exposure. The animals' body weights declined by 30%, urinary glucose, protein, and ketones became

abnormal, and succinic-dehydrogenase activity declined sharply in the kidney and rose sharply in the lung. Mortality among the rats exposed repeatedly to carbonyl fluoride was high (9 of 40), indicating that fluoride continued to be liberated by hydrolysis once in the body [Scheel et al. 1968b].

2. *Effects on Humans:* Carbonyl fluoride is a severe irritant of the eyes, skin, mucous membranes, and respiratory tract in humans. Its respiratory toxicity is believed to be equivalent to that of hydrogen fluoride [ACGIH 1993]. On repeated exposure, carbonyl fluoride inhibits succinic dehydrogenase activity, indicating that sublethal exposures are cumulative and that fluoride continues to be liberated after absorption into the body [Sittig 1985].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbonyl fluoride can cause pain, redness, and tearing of the eyes, eye or skin burns (corrosion), runny nose, coughing, pulmonary edema, and difficult breathing.

2. *Chronic exposure:* Carbonyl fluoride toxicity is similar to that caused in fluoride poisoning: respiratory distress, neurological abnormalities, gastrointestinal pain, muscular fibrillation, and skeletal fluorosis (excessive calcification of bone).

- **Emergency procedures**

> **WARNING!**
>
> **Exposed victims may die!**
> **Transport immediately to emergency medical facility**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* Severe burns and skin corrosion may result! If tissue is frozen, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If tissue is not frozen, ***immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbonyl fluoride and may result in worker exposures to this substance:

—Use in organic synthesis

—Thermal decomposition of polytetrafluoroethylene (Teflon, Fluon, etc.)

—Proposed use as a military poison gas

The following methods are effective in controlling worker exposures to carbonyl fluoride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbonyl fluoride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, respiratory system, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbonyl fluoride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbonyl fluoride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbonyl fluoride on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary fluoride concentration is a useful index of fluoride intake in workers; at an airborne concentration of 2.5 g/m^3 inorganic fluoride, average end-of-shift (8 hr) urinary concentrations are 4 mg fluoride per liter of urine. Some sources recommend an end-of-shift biological exposure index (BEI) of 10 mg fluoride per gram creatinine and a preshift BEI of 3 mg fluoride per gram creatinine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected phys-

iologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbonyl fluoride is determined by using a midget fritted-glass bubbler containing 10 ml 0.1N sodium hydroxide. Samples are collected at a recommended flow rate of 2.0 liter/min until a recommended air volume of 480 liters is collected. Analysis is conducted using an ion specific electrode. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If carbonyl fluoride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with carbonyl fluoride should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles carbonyl fluoride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbonyl fluoride is handled, processed, or stored.

STORAGE

Carbonyl fluoride should be stored in a cool, dry, well-ventilated area in tightly sealed, pressurized containers or holding tanks that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All piping systems in storage areas should be equipped with leak detection equipment to provide warning of leaks. Containers of carbonyl fluoride should be protected from physical damage and should be stored separately from moisture and heat.

LEAKS

In the event of a leak involving carbonyl fluoride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the leak.
5. For small spills, flush area with flooding amounts of water.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbonyl fluoride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbonyl fluoride is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will

expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbonyl fluoride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Carbonyl fluoride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U033. This substance has been banned from land disposal and may be treated by incineration. Carbonyl fluoride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbonyl fluoride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, boots, aprons, and gauntlets) should be worn to prevent any skin contact with carbonyl fluoride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing

materials to carbonyl fluoride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to carbonyl fluoride.

Safety glasses, goggles, or face shields should be worn during operations in which carbonyl fluoride might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbonyl fluoride. Contact lenses should not be worn if the potential exists for carbonyl fluoride exposure.

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ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CATECHOL

INTRODUCTION

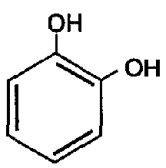
This guideline summarizes pertinent information about catechol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_6H_4(OH)_2$

- **Structure**



- **Synonyms**

  1,2-Benzenediol; pyrocatechol; o-dihydroxybenzene; pyrocatechin; o-diphenol; Durafur Developer C; o-hydroquinone; o-hydroxyphenol; oxyphenic acid; Pelagol Grey C; o-phenylenediol; pyrocatechinic acid

- **Identifiers**

  1. CAS No.: 120-80-9
  2. RTECS No.: UX1050000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Catechol is a colorless, crystalline solid that has a faint odor and sublimes easily.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 110.11
  2. Boiling point (760 mm Hg): 245.5°C (473.9°F)
  3. Specific gravity (water = 1): 1.344 at 40°C (104°F)
  4. Vapor density (air = 1 at boiling point of catechol): 3.79
  5. Melting point: 105°C (221°F)
  6. Vapor pressure at 118°C (244°F): 10 mm Hg
  7. Solubility: Soluble in water, ether, alcohol, hot benzene, and chloroform; very soluble in pyridine and acetone

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8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, flame, light, or air

2. Incompatibilities: Contact of catechol with strong oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving catechol.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to catechol; other sources rate catechol's fire hazard as slight.

1. Flash point: 127.2°C (261°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use water, dry chemical, or carbon dioxide to fight fires involving catechol.

Fires involving catechol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving catechol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for catechol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (20 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned catechol a threshold limit value (TLV) of 5 ppm (20 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of skin and respiratory tract irritation and central nervous system effects associated with exposure to catechol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to catechol can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Catechol is a potential corrosive to the eyes, nose, upper respiratory tract, and skin. Aqueous solutions of up to 55% (0.05 M) were not injurious when instilled into rabbits' eyes [Grant 1986]. Application of 100 mg of dry catechol onto rabbits' eyes caused erythematous and edematous conjunctiva, moderate exudate, and corneal opacities (Draize score 103/110) within 24 hr. The 72-hr evaluation revealed severe conjunctivitis, iritis, and diffuse corneal opacities (Draize score 78/110). On the 14th day, corneal vascularization, granulation, and conical protrusion were observed [Flickinger 1976]. Administration of catechol onto rabbit skin produced moderate erythema and slight edema of the intact sites while necrosis occurred at the abraded areas. Catechol was thereby classified as a primary irritant (Draize score 5.5/8.0) [Flickinger 1976]. The dermal LD_{50} in the rabbit is 800 mg/kg [NIOSH 1992b]. Rats tolerated an 8-hr inhalation exposure to 1,500 mg/m^3 catechol without visible effects, but exposure to 2,000 or 2,800 mg/m^3 caused tremors after 6 to 7 hr. The tremors disappeared following the first experimental day. In addition, the 2,000- and 2,800-mg/m^3

concentrations caused the animals to develop irritated and blackened extremities and tails. Two of six rats exposed to 2,000 mg/m^3 developed blackened tails of which the terminal one inch was lost (undefined). Six out of six rats exposed to 2,800 mg/m^3 had both blackened tails and toes. All lost the terminal inch of their tails, while several had missing toes. The author concluded that severe exposure could lead to necrosis and sloughing of peripheral tissues [Flickinger 1976]. Lethal oral doses have induced hyperemia of the stomach and intestines of rats [Clayton and Clayton 1981]. The lowest reported oral LD_{50}s for the rat and mouse are 260 and 260 mg/kg, respectively [NIOSH 1992b]. Large doses (amounts not specified) of catechol can cause depression of the central nervous system, a prolonged rise in blood pressure, and degenerative changes in the renal tubules. Deaths from lethal doses or exposures in animals are caused from respiratory failure [Clayton and Clayton 1981; ACGIH 1991]. Rabbits that received repeated sublethal oral doses (200 mg/kg) had altered sleep times, leukopenia, anemia, and methemoglobinemia [Clayton and Clayton 1981; NIOSH 1992b]. An in vitro micromass teratogen test confirmed that catechol inhibits cell differentiation of rat embryo midbrain and limb cells [Flint and Maclean 1988]. Conversely, in an in vivo Chernoff/Kavlock assay, rats received one oral dose of 333, 667, or 1,000 mg catechol/kg on day 11 of pregnancy. The lethality rates in dams were 1/15, 5/15, and 10/15, respectively. The two upper levels caused a statistically significant dose-related decrease in litter size and an increase in perinatal loss. The 333-, 667-, and 1,000-mg/kg dose levels induced a 23.1%, 66.7%, and 80% incidence of hind limb tetany and paralysis, short or kinky tails, and urogenital malformations in the pups, respectively [Kavlock 1990]. Catechol is mutagenic in bacterial and mammalian test systems [NIOSH 1992b]. Groups of 50 Swiss mice received 5 g benzo(a)pyrene [B(a)P] with or without 2-mg catechol in acetone, three times per week for 52 weeks. Catechol plus B(a)P significantly increased the number of squamous cell carcinomas of the skin (31) when compared to benzo(a)pyrene alone (10), acetone controls (0), or negative controls (0). The rate of skin papillomas per affected mouse was also tripled when catechol plus B(a)P were administered. Catechol alone was not investigated in this study [IARC 1977]. When 2-mg catechol were suspended in 10-mg cholesterol pellets and implanted into the urinary bladders of mice for 25 weeks, a significant increase ($p=0.03$) in undefined carcinomas was induced above the control incidence [IARC 1977]. IARC found no adequate human studies and inadequate evidence of carcinogenic potential for the above animal studies. They classified it as a Group 3 chemical: The agent is not classifiable as to its carcinogenicity to humans [IARC 1977].

2. *Effects on Humans:* In humans, catechol is an eye and skin irritant, a skin sensitizer, and a depressant of the central nervous system. Catechol also causes eye burns that are slow to heal [Grant 1986]. Contact of catechol with the skin causes an eczematous dermatitis in sensitized workers. Absorption through the skin has resulted in signs and symptoms of illness resembling those of phenol poisoning, except that catechol-induced convulsions are more severe than those caused by phenol poisoning [ACGIH 1991]. Catechol is mutagenic in human test systems [NIOSH 1992b].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to catechol can cause redness, pain, and tearing of the eyes, runny nose, scratchy throat, and difficult breathing. Contact of catechol with the eyes may cause burns and permanent impairment of vision. Severe overexposure may cause convulsions.

2. *Chronic exposure:* Continued low-level exposure to catechol can cause eczematous dermatitis, with red, raised, and oozing areas of the skin.

- **Emergency Procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* If particulates, mists, or vapors of catechol are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if catechol or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve catechol and result in worker exposures to this substance:

—Use as an intermediate in the manufacture of 4-tertiary-butyl-catechol and certain chlorinated dibenzo-para-dioxins

—Use as a constituent of polymerization inhibitors and antioxidants

—Use in electro-sensitive copying papers, in photography, and in rubber compounding

—Use as a photographic developer, as an oxidation base in hair dye preparations, and as an analytical reagent

—Use as an antiseptic

—Use in the manufacture of specialty inks and light stabilizers

The following methods are effective in controlling worker exposures to catechol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to catechol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to catechol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory system or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to catechol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of catechol on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although catechol can be measured in the urine of exposed individuals, no correlation between urinary and airborne catechol concentrations has yet been established. Therefore, no biological monitoring test acceptable for routine use is available for catechol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne catechol is determined by using an XAD-7 tube (100/50-mg sections, 15/50 mesh). Samples are collected at a recommended flow rate of 0.1 liter/min until a recommended air volume of 24 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If catechol contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with catechol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of catechol, particularly its potential to cause eye and skin burns on contact.

A worker who handles catechol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where catechol or a solution containing catechol is handled, processed, or stored.

STORAGE

Catechol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of catechol should be protected from physical damage and should be stored separately from strong oxidizers, light, heat, sparks, and open flame. Because containers that formerly contained catechol may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving catechol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill.
5. Avoid raising dust during cleanup.
6. Sweep or vacuum the spilled material and gently place into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Catechol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of catechol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or otherwise use 10,000 lb or more of catechol per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of catechol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although catechol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this

substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of catechol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with catechol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to catechol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to catechol.

If catechol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which catechol might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with catechol. Contact lenses should not be worn if the potential exists for catechol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CELLULOSE

INTRODUCTION

This guideline summarizes pertinent information about cellulose for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $(C_6H_{10}O_5)_n$

- **Synonyms**

  Abicel; β-Amylose; Avicel; α-Cellulose; Cellex MX; Arbocel; Cupricellulose; Cellulose 248; Hydroxycellulose; Pyrocellulose; Sulfite cellulose

- **Identifiers**

  1. CAS No.: 9004-34-6
  2. RTECS No.: FJ5691460
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Cellulose is the principal fiber cell wall material of green terrestrial and marine plants; it is the most abundant polysaccharide produced in nature. Cellulose is a white substance that is odorless and tasteless. Natural cellulose exists both in microcrystalline and nonfibrous forms.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 300,000 to greater than 1,000,000 depending on the degree of polymerization of the particular cellulose
  2. Boiling point: Not applicable
  3. Specific gravity (water = 1): 1.27 to 1.61
  4. Vapor density: Not applicable
  5. Melting point: 260° to 270°C (500° to 518°F) (decomposes)
  6. Vapor pressure: Not applicable
  7. Solubility: Insoluble in water and organic solvents; dissolved by concentrated zinc chloride solutions, by ammoniacal copper hydroxide solutions, and by caustic alkali with carbon disulfide
  8. Evaporation rate: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Reactivity**

  1. Conditions contributing to instability: Heat or moisture

  2. Incompatibilities: Contact of cellulose with water, bromine pentafluoride, sodium nitrate, or fluorine may cause fires and violent explosions.

  3. Hazardous decomposition products: Toxic gases and particulates (such as carbon monoxide and carbon dioxide) may be released in a fire involving cellulose.

  4. Special precautions: None reported

- **Flammability**

  The National Fire Protection Association has not assigned a flammability rating to cellulose; however, cellulose is combustible and may be flammable under certain conditions.

  1. Flash point: Data not available

  2. Autoignition temperature: Data not available

  3. Flammable limits in air: Data not available

  4. Extinguishant: Use water to fight fires involving cellulose.

  Fires involving cellulose should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cellulose.

EXPOSURE LIMITS

- **OSHA PEL**

  The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cellulose is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

  The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

  The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cellulose (total dust) a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

  The OSHA and ACGIH limits are based on the risk of local irritant effects associated with exposure to cellulose.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

  Exposure to cellulose can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

  1. *Effects on Animals:* There are no acute or chronic toxicity studies in animals for cellulose.

  2. *Effects on Humans:* Like all dusts, cellulose dust produces mechanical irritation of the eyes, skin, or mucous membranes if it contacts these tissues in excessive amounts; there are no reports of other exposure-related effects of cellulose in humans.

- **Signs and symptoms of exposure**

  1. *Acute exposure:* No signs or symptoms of acute exposure to cellulose, other than those of local irritation, have been reported.

  2. *Chronic exposure:* No signs or symptoms of chronic exposure to cellulose have been reported.

- **Emergency procedures**

> **WARNING**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of cellulose is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cellulose and may result in worker exposures to this substance:

—Manufacture of paper, fillers, cellophane, and rayon in the textile and paper industries

—Production of chemical derivatives such as certain explosives

—Use as a source of ethanol (enzymatic hydrolysis) and methanol (destructive distillation of wood)

—Use in the food industry to produce stabilizers, thickeners, and texturizers and in fillings and meringue

—Generated during wood processing and logging

The following methods are effective in controlling worker exposures to cellulose, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or

other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cellulose, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cellulose at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cellulose exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cellulose on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cellulose.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cellulose (total dust) is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5 microns). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by the gravimetric (weighing) method. This method has a sampling and analytical error of 0.10 and is described in the OSHA Computerized Information System [OSHA 1989], the *OSHA Chemical Information Manual* [OSHA 1987], and in NIOSH Method No. 0500 in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

A worker's exposure to airborne cellulose (respirable fraction) is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5 microns) preceded by a 10-mm nylon cyclone. Samples are collected at a maximum flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by the gravimetric (weighing) method. This method has a sampling and analytical error of 0.10 and is described in the OSHA Computerized Information System, the *OSHA Chemical Information Manual*, and in NIOSH Method No. 0600 in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If a large amount of cellulose dust collects on the skin, workers should wash the affected areas with soap and water.

Clothing excessively contaminated with cellulose should be removed to avoid local irritation of the skin.

A worker who handles cellulose should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cellulose is handled, processed, or stored.

STORAGE

Cellulose should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of cellulose should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving cellulose, the following steps should be undertaken: use a clean shovel and place the material into a clean, dry container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cellulose is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cellulose; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cellulose emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cellulose is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cellulose exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the

requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged contact of the skin with cellulose dust. Safety glasses, goggles, or face shields should be worn during operations in which cellulose might contact the eyes (e.g., through dust particles).

REFERENCES CITED

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CESIUM HYDROXIDE

INTRODUCTION

This guideline summarizes pertinent information about cesium hydroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CsOH

- **Synonyms**

  Cesium hydrate; cesium hydroxide dimer; cesium hydroxide, solid; cesium hydroxide, solution

- **Identifiers**

  1. CAS No.: 21351-79-1
  2. RTECS No.: FK9800000
  3. DOT UN: 2682 60 (solid); 2681 60 (solution)
  4. DOT label: Corrosive

- **Appearance and odor**

  Cesium hydroxide is a noncombustible, colorless or yellowish, deliquescent, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 149.92
  2. Boiling point: Data not available
  3. Specific gravity (water = 1): 3.68
  4. Vapor density: Data not available
  5. Melting point: 272.3°C (522.1°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Very soluble in water (generates heat); soluble in alcohol
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Cesium hydroxide is a strong base; in contact with water or moisture, it causes the generation of considerable heat.
  2. Incompatibilities: Contact of cesium hydroxide with

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acids, many organic compounds, many metals (such as aluminum, lead, tin, or zinc), glass, oxygen, or carbon dioxide causes a violent reaction.

3. Hazardous decomposition products: None reported

4. Special precautions: Cesium hydroxide must be stored in silver or platinum and out of contact with air because of its reactivity with glass and carbon dioxide.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for cesium hydroxide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to extinguish fires involving cesium hydroxide.

Fires involving cesium hydroxide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of cesium hydroxide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cesium hydroxide. Structural firefighters' protective clothing may provide limited protection against fires involving cesium hydroxide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cesium hydroxide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cesium hydroxide a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of eye irritation associated with exposure to cesium hydroxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cesium hydroxide can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cesium hydroxide is irritating and corrosive to the eyes, mucous membranes, skin, and upper respiratory tract; the severity of these effects depends on the concentration of cesium hydroxide. Application of 5 mg cesium hydroxide to the eye of rabbits for 5 min, followed by rinsing with water, caused severe eye irritation; application of 5 mg to the skin of rabbits for 24 hr caused mild skin irritation [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50} for cesium hydroxide in the rat is 570 mg/kg, and the intraperitoneal LD_{50} in the same species is 100 mg/kg [NIOSH 1993]. The oral LD_{50} in mice is 800 mg/kg [NIOSH 1993; Sax and Lewis 1989; ACGIH 1991].

2. *Effects on Humans:* In humans, cesium hydroxide is irritating and corrosive to the eyes, nose, throat, and skin. Solutions containing 5% cesium hydroxide are regarded as safe for human skin contact; however, in contact with the eyes, a solution of this concentration causes extreme irritation and corneal corrosion [Sittig

1985]. Stronger solutions of cesium hydroxide cause eye and skin burns and may cause permanent damage. There is no other toxicological information on the effects of exposure to cesium hydroxide in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute inhalation exposure to cesium hydroxide include a burning sensation in nose, throat, and upper respiratory tract; runny nose; pain, redness and tearing of the eyes; difficult breathing; and redness, pain, and burns of the skin.

2. *Chronic exposure:* No signs or symptoms of continued low-level exposure to cesium hydroxide have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately*** but ***gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cesium hydroxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

   NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve cesium hydroxide and may result in worker exposures to this substance:

—Use as an electrolyte in alkaline storage batteries at subzero temperatures

—Use as a polymerization catalyst for siloxanes

—Use as an agent in the removal of sulfur from heavy oils

—Use as a raw material in the production of cesium salts, which are then used to produce cesium metal for electronic devices

The following methods are effective in controlling worker

exposures to cesium hydroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cesium hydroxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cesium hydroxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cesium hydroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cesium hydroxide on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitor-

ing test acceptable for routine use has yet been developed for cesium hydroxide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cesium hydroxide is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Elemental cesium analysis is conducted by atomic absorption spectroscopy, and the results are reported as cesium hydroxide. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cesium hydroxide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cesium hydroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cesium hydroxide, particularly its potential to cause eye and skin burns.

A worker who handles cesium hydroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cesium hydroxide or a solution containing cesium hydroxide is handled, processed, or stored.

STORAGE

Cesium hydroxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Cesium hydroxide should not be stored in glass containers. Containers of cesium hydroxide should be protected from physical damage and should be stored separately from acids, organic compounds, metals, oxygen, carbon dioxide, moisture, heat, sparks, and open flame. Because containers that formerly contained cesium hydroxide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cesium hydroxide or a solution containing cesium hydroxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Do not use water in clean-up.

4. For small dry spills, use a scoop or clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

5. For liquid spills, dilute the concentration of cesium hydroxide with water, neutralize the spilled material with dilute acid, absorb with sand or other noncombustible absorbent material, and place into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Cesium hydroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cesium hydroxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cesium hydroxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cesium hydroxide is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. D002. This substance has been banned from land disposal and may be treated by deactivation.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cesium hydroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cesium hydroxide. Rubber gloves, rubber aprons, or protective suits and rubber boots should be worn when needed to prevent contact with cesium hydroxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under

actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cesium hydroxide permeation; however, neoprene and polyvinyl-chloride have been tested against chemically similar materials (sodium hydroxide and potassium hydroxide) and may provide greater than 8-hr of resistance to permeation. Since specific test data are not available for cesium hydroxide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cesium hydroxide.

If cesium hydroxide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cesium hydroxide might contact the eyes (e.g., through splashes of solutions containing cesium hydroxide). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cesium hydroxide. Contact lenses should not be worn if the potential exists for cesium hydroxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROACETYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about chloroacetyl chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_2H_2Cl_2O$

- **Structure**

  $ClCH_2COCl$

- **Synonyms**

  Chloroacetic acid chloride; chloroacetic chloride; monochloroacetyl chloride; chloracetyl chloride

- Identifiers

  1. CAS No.: 79-04-9
  2. RTECS No.: AO6475000
  3. DOT UN: 1752 59
  4. DOT label: Corrosive

- **Appearance and odor**

  Chloroacetyl chloride is a colorless to slightly yellow liquid with a strong, pungent odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 112.94
  2. Boiling point (760 mm Hg): 105° to 110°C (221° to 230°F)
  3. Specific gravity (water = 1): 1.42 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chloroacetyl chloride): Data not available
  5. Melting point (at 760 mm Hg): 106°C (222.8°F)
  6. Freezing point: -22.5°C (-8.5°F)
  7. Vapor pressure at 21°C (69.8°F): 20 mm Hg
  8. Solubility: Insoluble in water; soluble in ether and acetone
  9. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and water
  2. Incompatibilities: Contact of chloroacetyl chloride

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with water causes decomposition and the release of hydrogen chloride gas and chloroacetic acid; avoid contact with alcohols, amines, and alkalis.

3. Hazardous decomposition products: Toxic gases (such as hydrogen chloride, phosgene, and chlorine) may be released in a fire involving chloroacetyl chloride.

4. Special precautions: Keep chloroacetyl chloride away from moisture or water.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloroacetyl chloride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire. Do not use water.

Fires involving chloroacetyl chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloracetyl chloride should be moved from the fire area if it is possible to do so safely. If this is not possible, cool fire-exposed containers from the sides with water until well after the fire is out. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloroacetyl chloride. Chemical protective clothing that is specifically recommended for chloroacetyl chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloroacetyl chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chloroacetyl chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.2 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloroacetyl chloride a threshold limit value (TLV) of 0.05 ppm (0.23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 0.15 ppm (0.69 mg/m^3) for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 minutes. The ACGIH has also assigned a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of skin and respiratory irritation associated with choloracetyl chloride exposure. The ACGIH limits are based on the risk of eye, skin, and respiratory irritation and systemic effects associated with exposure to chloroacetyl chloride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloroacetyl chloride can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloroacetyl chloride is highly corrosive to tissues; in animals it affects the lungs, eyes, and skin. In rabbits the dermal LD_{50} is 178 mg/kg and the dermal LD_{LO} ranges from 316 to 501 mg/kg [AIHA 1987; NIOSH 1989; ACGIH 1991]. The LC_{50} in the rat is 1,000 ppm for a 4-hr exposure [NIOSH 1989]. A 5 to 10 min exposure to a

concentration of 4 ppm caused respiratory difficulty in rats, but no effect was observed from the inhalation of a 2.5-ppm chloroacetyl chloride concentration for 7 hr [NLM 1992; AIHA 1987]. A 30-day inhalation study with rats, mice, and hamsters showed that these animals develop eye and respiratory irritation at an airborne concentration of 2.5 ppm [NLM 1992]. The oral LD_{50} in the rat is 120 mg/kg; cough and dermatitis were noted before death [NIOSH 1989].

2. *Effects on Humans:* In humans, chloroacetyl chloride is corrosive to the skin and eyes and affects the respiratory system [Sittig 1985]. The effects of acute workplace exposure include mild to moderate skin irritation and burns, lacrimation, mild eye burns, mild to moderate respiratory effects with cough, dyspnea, cyanosis, and mild gastrointestinal effects [ACGIH 1991; AIHA 1987]. Respiratory effects include coughing, difficult breathing, and oxygen insufficiency [ACGIH 1991a]. Workers exposed to peak chloroacetyl chloride concentrations of 140 ppb developed eye irritation and reported experiencing minimal respiratory irritation [NLM 1992]. In an industrial accident, a worker was drenched by a mixture containing chloroacetyl chloride, xylidine, benzene, and sodium carbonate. Although immediately put under a shower, he suffered extensive first- and second-degree burns, developed pulmonary edema, and had three episodes of cardiac arrest during emergency treatment. He went into a coma that lasted several weeks; the ultimate outcome of this case is not reported [ACGIH 1991; NLM 1992]. Workers involved in the rescue of this employee suffered blisters on their hands and complained of tightness of the chest and slight nausea for as long as 2 days after the incident [NLM 1992]. Most of the acute effects experienced by this worker are believed to have been caused by the chloroacetyl chloride.

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute inhalation overexposure to chloroacetyl chloride include pain, redness, and tearing of the eyes, sore throat, pain in the chest, fluid in the lungs, and difficult breathing. Contact with the liquid can cause severe skin or eye burns.

2. *Chronic exposure:* The signs and symptoms of continued low-level exposure to chloroacetyl chloride may include a burning sensation in the upper respiratory tract, wheezing, laryngitis, and shortness of breath.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of chloroacetyl chloride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloroacetyl chloride or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloroacetyl chloride and may result in worker exposures to this substance:

—Manufacture of herbicides (such as alachlor, allidochlor, butachlor, and others) and tear gas

—Use as an intermediate in the manufacture of chloroacetophenone and other chemicals

—Manufacture of pharmaceuticals, such as chlordiazepoxide hydrochloride, diazepam, lidocaine, and mianserin

The following methods are effective in controlling worker exposures to chloroacetyl chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Personal protective equipment and local ventilation are a necessity at chloroacetyl chloride transfer points where leakage can be expected.

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chloroacetyl chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloroacetyl chloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloroacetyl chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloroacetyl chloride on the respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloroacetyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chloroacetyl chloride is determined by using a XAD-2 tube coated with 1- (2-pyridyl)piperazine. Samples are collected at a recommended flow rate of 0.05 liter/min until a recommended air volume of 10 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If chloroacetyl chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with chloroacetyl chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chloroacetyl chloride, particularly its potential to cause eye and skin burns.

A worker who handles choloroacetyl chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloroacetyl chloride or a solution containing chloroacetyl chloride is handled, processed, or stored.

STORAGE

Chloroacetyl chloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chloroacetyl chloride should be protected from physical damage and should be stored separately from water, steam, surface moisture, oxidizing agents, strong bases, alcohols, heat, sparks, and open flame. Because containers that formerly contained chloroacetyl chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloroacetyl chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the chloroacetyl chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloroacetyl chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloroacetyl chloride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chloroacetyl chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chloroacetyl chloride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloroacetyl chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of

an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with chloroacetyl chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chloroacetyl chloride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chloroacetyl chloride.

If chloroacetyl chloride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloroacetyl chloride might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloroacetyl chloride.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLORODIFLUOROMETHANE

INTRODUCTION

This guideline summarizes pertinent information about chlorodifluoromethane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CHClF_2$

- **Synonyms**

  Algeon 22; CFC 22; difluorochloromethane; difluoromonochloromethane; Dymel 22; Fluorocarbon-22; Freon 22; Genetron 22; monochlorodifluoromethane; refrigerant 22; Ucon 22

- **Identifiers**

  1. CAS No.: 75-45-6
  2. RTECS No.: PA6390000
  3. DOT UN: 1018 12
  4. DOT label: Nonflammable gas

- **Appearance and odor**

  Chlorodifluoromethane is a colorless, odorless, nonflammable gas; however, it may be shipped as a liquefied gas under pressure or reduced temperature.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 86.47
  2. Boiling point (760 mm Hg): -40.8°C (-41.4°F)
  3. Specific gravity (water = 1): 1.49 at -69°C (-92.2°F)
  4. Vapor density (air = 1 at boiling point of chlorodifluoromethane): 2.98
  5. Melting point: -146°C (-230.8°F)
  6. Vapor pressure at 21°C (70°F): 7,121.2 mm Hg
  7. Solubility: Very soluble in water; soluble in ether, acetone, and chloroform
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: Contact of chlorodifluoromethane at high temperatures with alkalies or alkaline earth

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metals such as aluminum, sodium, potassium, or zinc causes thermal decomposition.

3. Hazardous decomposition products: Toxic gases (such as fluorine, chlorine, phosgene, and carbonyl halides) may be released in a fire involving chlorodifluoromethane.

4. Special precautions: Corrosion can occur when magnesium alloys or aluminum containing more than 2% magnesium is used with fluorocarbon systems in which water may be present.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to chlorodifluoromethane; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving chlorodifluoromethane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chlorodifluoromethane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorodifluoromethane. Structural firefighters' protective clothing may provide limited protection against fires involving chlorodifluoromethane.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chlorodifluoromethane [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1,000 ppm (3,500 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 1,250 ppm (4,375 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure limit that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorodifluoromethane a threshold limit value (TLV) of 1,000 ppm (3,540 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of cardiac sensitization, asphyxiation, and central nervous system effects associated with exposure to chlorodifluoromethane.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorodifluoromethane can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chlorodifluoromethane causes depression of the central nervous system, cardiac arrhythmias, and asphyxiation. The LC_{50} in the rat is 35 parts per hundred (pph) (350,000 ppm) for a 15-min exposure; acutely poisoned animals exhibited altered sleep times, stumbling, and respiratory depression before death [NIOSH 1989]. Mice exposed for 2-hr periods showed a maximum tolerated concentration of 320,000 ppm, and a minimum fatal level of 370,000 ppm [ACGIH 1991]. Rats and guinea pigs exposed by inhalation to airborne concentrations of 75,000 to 100,000 ppm chlorodifluoromethane for 2-hr showed excitation and/or changes in equilibrium; narcosis occurred at 200,000 ppm and death occurred at 300,000 and

400,000 ppm [ACGIH 1991]. Dogs exposed to a 50,000-ppm concentration of chlorodifluoromethane developed cardiac sensitization; exposure to 25,000 ppm did not cause this effect [ACGIH 1991]. The minimum concentration capable of altering the reflex response in rabbits varied between 11,000 and 20,000 ppm [ACGIH 1991]. In 2-hr exposures to guinea pigs, the highest concentration tested (200,000 ppm) did not cause death, while 50,000 ppm produced mild clinical changes, and minimal effects were noted at 25,000 ppm [ACGIH 1991]. In a 4-week study in which rats, guinea pigs, dogs, and cats were exposed to a 50,000-ppm concentration of chlorodifluoromethane for twenty 3.5-hr episodes, no clinical, biochemical, or pathological effects were observed [ACGIH 1991]. Rats, mice, and rabbits were exposed for 6 hr/day, 6 days/week for 10 months to 14,000 ppm chlorodifluoromethane. In another experiment, rats and mice were exposed to 2,000 ppm of this substance for the same period. No effects were noted in animals exposed at the lower concentration, but at 14,000 ppm, alterations occurred in body weight, physiological endurance, and hematological characteristics; pathological changes were noted in the lungs, central nervous system, heart, liver, kidneys, and spleen [ACGIH 1991]. In one inhalation bioassay in rats, males exposed to the highest concentration administered showed only a marginal increase in the incidence of subcutaneous fibrosarcomas and Zymbal-gland tumors, and negative results were obtained for females [IARC 1987]. Based on this study, the International Agency for Research on Cancer (IARC) has concluded that the evidence for chlorodifluoromethane's carcinogenicity in animals is limited [IARC 1987].

2. *Effects on Humans:* In humans, chlorodifluoromethane can affect the heart; at very high concentrations, it is an asphyxiant. A study of hospital personnel exposed to 300 ppm chlorodifluoromethane during tissue freezing procedures revealed a 3.5-fold increase in the incidence of palpitations in exposed individuals over the incidence in nonexposed hospital personnel [Clayton and Clayton 1981; Hathaway et al. 1991]. An epidemiologic study involving workers exposed to chlorofluorocarbons, including chlorodifluoromethane, showed no increased mortality due to heart, circulatory, or malignant disorders [Hathaway et al. 1991]. A small study of 539 refrigeration workers exposed to a mixture of chlorofluorocarbons, including chlorodifluoromethane, for at least 6 months and followed for up to 30 years was inconclusive, leading IARC to conclude that the evidence for the carcinogenicity of this substance in humans is inadequate [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Chlorodifluoromethane may cause dizziness, disorientation, incoordination, narcosis, nausea, vomiting, heart palpitations (irregular heart beat), tightness in the chest, and difficult breathing. Direct tissue contact with liquid chlorodifluoromethane may cause frostbite.

2. *Chronic exposure:* Continued low-level exposure to chlorodifluoromethane may cause an irregular heartbeat.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of frostbite, toxicity, or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* If tissue is frozen, seek medical attention ***immediately***; do not rub the affected areas or flush them with water. If tissue is not frozen, immediately and thoroughly wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from fur-

ther exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorodifluoromethane and may result in worker exposures to this substance:

—Formulation of aerosol propellants (former use)

—Use as a component of fluorocarbon resins (such as tetrafluoroethylene polymers) and as a low-temperature solvent

—Use in central air conditioning systems and heat pumps

—Use in cylinder packing and shipping and tank car filling

The following methods are effective in controlling worker exposures to chlorodifluoromethane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chlorodifluoromethane, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the cardiovascular system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorodifluoromethane at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and

other findings consistent with diseases of the cardiovascular system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorodifluoromethane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorodifluoromethane on the cardiovascular system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chlorodifluoromethane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorodifluoromethane is determined by using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.05 liter/min or less until a maximum air volume of 1 liter is collected. The sample is then treated with carbon disulfide to extract the chlorodifluoromethane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1991].

PERSONAL HYGIENE

If liquid chlorodifluoromethane contacts the skin, workers should flush the affected areas immediately with plenty of tepid water for 15 min, and then wash with soap and water.

Clothing contaminated with liquid chlorodifluoromethane should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles cylinders of liquid chlorodifluoromethane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorodifluoromethane is handled, processed, or stored.

STORAGE

Chlorodifluoromethane should be stored in a cool, dry, well-ventilated area in closed, pressurized, steel containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chlorodifluoromethane should be protected from physical damage and should be stored separately from alkaline earth metals (such as sodium, aluminum, or potassium), heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorodifluoromethane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chlorodifluoromethane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chlorodifluoromethane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorodifluoromethane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chlorodifluoromethane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorodifluoromethane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with liquid chlorodifluoromethane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against chlorodifluoromethane and have demonstrated resistance: Natural rubber and neoprene. Nitrile, polyvinylchloride, and styrene-butadiene rubber have demonstrated poor resistance to permeation by chlorodifluoromethane.

If liquid chlorodifluoromethane is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which liquid chlorodifluoromethane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with liquid chlorodifluoromethane. Contact lenses should not be worn if the potential exists for chlorodifluoromethane exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROPENTAFLUOROETHANE

INTRODUCTION

This guideline summarizes pertinent information about chloropentafluoroethane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CClF_2CF_3$

- **Synonyms**

  F-115; Fluorocarbon-115; Freon 115; Genetron 115; Halocarbon 115; monochloropentafluoroethane

- **Identifiers**

  1. CAS No.: 76-15-3
  2. RTECS No.: KH7877500
  3. DOT UN: 1020 12
  4. DOT label: Nonflammable gas

- **Appearance and odor**

  Chloropentafluoroethane is a colorless, odorless, nonflammable gas; it is shipped as a liquefied gas under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 154.47
  2. Boiling point (760 mm Hg): -39.1°C (-38.4°F)
  3. Specific gravity: 5.5 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: -106°C (-222.8°F)
  6. Vapor pressure at 21.1°C (69.8°F): 6,034.4 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol and ether
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: Contact of chloropentafluoroethane at high temperatures with alkalies or alka-

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

line earth metals such as powdered aluminum, potassium or zinc causes thermal decomposition.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrochloric or hydrofluoric acid, phosgene, fluorides, and chlorides) may be released in a fire involving chloropentafluoroethane.

4. Special precautions: Corrosion can occur when magnesium alloys or aluminum containing more than 2% magnesium is used with fluorocarbon systems in which water may be present.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for chloropentafluoroethane; this substance is a nonflammable gas.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical or carbon dioxide to fight fires involving chloropentafluoroethane.

Fires involving chloropentafluoroethane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloropentafluoroethane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloropentafluoroethane. Structural firefighters' protective clothing may provide limited protection against fires involving chloropentafluoroethane.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chloropentafluoroethane [29 CFR 1910.1000, Table Z-1].

- **NIOSH PEL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1,000 ppm (6,320 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloropentafluoroethane a threshold limit value (TLV) of 1,000 ppm (6,320 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cardiac, skin, CNS, and respiratory effects associated with exposure to chloropentafluoroethane [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloropentafluoroethane can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chloropentafluoroethane affects the heart and respiratory system at very high doses. Early studies in experimental animals showed that inhalation of a chloropentafluoroethane concentration of approximately 200,000 ppm caused confusion, pulmonary irritation, tremors, and, occasionally, coma [NLM 1992]. At a concen-

tration of 190,000 ppm, chloropentafluoroethane caused cessation of respiration (apnea) in rats exposed from 4 to 26 min [NLM 1992]. Rats exposed at 800,000 ppm plus 20% oxygen for 4 hr showed no clinical effects of histopathology. Rats and guinea pigs exposed at 600,000 ppm chloropentafluoroethane in oxygen for 2 hr and guinea pigs exposed at 200,000 ppm chloropentafluoroethane in air for varying intervals up to 2 hr showed no adverse clinical signs [ACGIH 1991]. Studies with anesthetized dogs, rats, and monkeys showed that, under certain conditions, exposures of 100,000 to 200,000 ppm of chloropentafluoroethane may increase blood pressure, accelerate heart rate, cause myocardial depression, or change pulmonary mechanics [ACGIH 1991]. Species differences in sensitivity are great. Monkeys do not show respiratory or circulatory effects when exposed to a 200,000 ppm concentration of chloropentafluoroethane; dogs show no respiratory depression when exposed to 200,000 ppm but do show bronchoconstriction, decreased compliance, sensitization of the heart to epinephrine, tachycardia, myocardial depression, and hypotension when inhaling 100,000 to 250,000 ppm chloropentafluoroethane; rats show bronchospasm, decreased compliance, and respiratory stimulation after inhalation of 100,000 ppm chloropentafluoroethane [Clayton and Clayton 1981; NLM 1992]. Rats, mice, rabbits, and dogs which received 90 exposures, 6 hr daily to 100,000 ppm chloropentafluoroethane showed no adverse effects, and rats, guinea pigs, dogs, and cats exposed to 200,000 ppm chloropentafluoroethane for 3.5 hr/day, 5 days/week for 4 weeks also showed no adverse effects after the cessation of exposure [ACGIH 1991].

2. *Effects on Humans:* In humans, chloropentafluoroethane can affect the heart, central nervous system, and skin. The neurological effects of chlorofluorocarbon exposure were evaluated in 27 refrigeration repair workers and 14 age-matched control workers from a local union of plumbers, pipefitters, and insulation workers. Personal air samples taken on two worker-participants over the course of a typical workshift showed average exposures of 1.4 ppm chlorodifluoromethane and 2.2 ppm chloropentafluoroethane. No peripheral neuropathy was seen among the study subjects, and there was no significant difference in mean nerve conduction velocities between study and reference subjects; however, lightheadedness and palpitations were reported significantly more often by refrigeration repair workers than by controls [NLM 1992]. The defatting effects of fluorocarbons such as chloropentafluoroethane, when in prolonged or repeated contact with the skin, may cause dermatologic problems, and contact of the skin with liquefied chloropentafluoroethane may cause frostbite [Clayton and Clayton 1981; Braker and Mossman 1980].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to chloropentafluoroethane include difficult breathing, dizziness, disorientation, incoordination, narcosis, and nausea or vomiting. Exposure to very high concentrations of this substance may affect the heart, causing irregular heartbeat, which could cause death. Contact of the skin with the evaporating liquid may cause frostbite.

2. *Chronic exposure:* The signs and symptoms of chronic exposure of the skin to chloropentafluoroethane include defatting and dermatitis.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of frostbite, toxicity, or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* If tissue is frozen, seek medical attention ***immediately;*** do not rub the affected areas or flush them with water. If tissue is not frozen, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloropentafluoroethane and may result in worker exposures to this substance:

—Use as a refrigerant in home appliances, mobile air conditioning units, and retail food refrigeration systems and chillers

—Use as a chemical intermediate

The following methods are effective in controlling worker exposures to chloropentafluoroethane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chloropentafluoroethane, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, cardiovascular system, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloropentafluoroethane at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and

other findings consistent with diseases of the skin, cardiovascular system, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloropentafluoroethane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloropentafluoroethane on the skin, cardiovascular system, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloropentafluoroethane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chloropentafluoroethane is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.05 liter/min until a recommended air volume of 2.5 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If liquid chloropentafluoroethane contacts the skin, watch for the development of frostbite. If frostbite occurs, the affected part should be wrapped in woolen material and should then be immersed in warm water until medical help is obtained.

Clothing contaminated with liquid chloropentafluoroethane should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles chloropentafluoroethane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where chloropentafluoroethane is handled, processed, or stored.

STORAGE

Chloropentafluoroethane should be stored in a cool, dry, well-ventilated area in tightly sealed, pressurized containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chloropentafluoroethane should be protected from physical damage and should be stored separately from metals, including aluminum, zinc, and beryllium, heat, sparks, and open flame.

LEAKS

In the event of a leak involving chloropentafluoroethane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the leak.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloropentafluoroethane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloropentafluoroethane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chloropentafluoroethane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chloropentafluoroethane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloropentafluoroethane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with chloropentafluoroethane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chloropentafluoroethane permeation; however, the following materials have been tested against chemically similar materials (Freon 113) and have withstood permeation for periods greater than 8 hr: nitrile rubber and Teflon®. Since specific test data are not available for chloropentafluoroethane, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chloropentafluoroethane.

Safety glasses, goggles, or face shields should be worn during operations in which liquid chloropentafluoroethane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloropentafluoroethane. Contact lenses should not be worn if the potential exists for chloropentafluoroethane exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLORPYRIFOS

INTRODUCTION

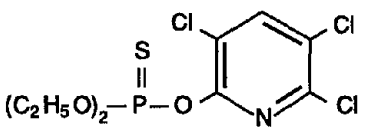
This guideline summarizes pertinent information about chlorpyrifos for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{11}Cl_3NO_3PS$

- **Structure**



- **Synonyms**

Brodan; chloropyrifos-ethyl; O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate; DOWCO 179; Dursban; Lorsban; Pyrinex

- **Identifiers**

1. CAS No.: 2921-88-2
2. RTECS No.: TF6300000
3. DOT UN: 2783 55
4. DOT label: None

- **Appearance and odor**

Chlorpyrifos is a colorless to white, crystalline solid with a mild, mercaptan-like odor. The technical grade often contains volatile contaminants, which are partly responsible for the offensive odor of this substance. Chlorpyrifos is an organophosphate insecticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 350.57
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.398 at 43.5°C (110.3°F) (liquid)
4. Vapor density: Data not available
5. Melting point: 41° to 42°C (105.8° to 107.6°F)
6. Vapor pressure at 25°C (77°F): 0.00002 mm Hg
7. Solubility: Slightly soluble in water; soluble in most organic solvents; slowly hydrolyzed by acid or alkaline solutions
8. Evaporation rate: Data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of chlorpyrifos with strong acids (such as hydrochloric, sulfuric, or nitric acid) causes a violent reaction. Contact with acidic or alkaline solutions causes hydrolysis.

3. Hazardous decomposition products: Toxic gases (such as chlorine and the oxides of nitrogen, phosphorus, and sulfur) may be released in a fire involving chlorpyrifos.

4. Special precautions: Chlorpyrifos is corrosive to copper and brass.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to chlorpyrifos; however, this substance is combustible.

1. Flash point: 27.8°C (82°F)(Dursban®); 30.6°C (87°F)(Lorsban)(TAG closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving chlorpyrifos.

Fires involving chlorpyrifos should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chlorpyrifos may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Do not scatter this material. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorpyrifos. Chemical protective clothing that is specifically recommended for chlorpyrifos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chlorpyrifos.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chlorpyrifos [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.6 mg/m^3 as a short-term exposure limit (STEL). The STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday. The NIOSH REL also bears a Skin notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorpyrifos a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to chlorpyrifos [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to chlorpyrifos.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorpyrifos can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chlorpyrifos is an inhibitor of blood and plasma cholinesterase. The dermal LD_{50} in rabbits is 2,000 mg/kg, and the oral LD_{50} in rats is 82 mg/kg [NIOSH 1990]. Administered to monkeys at doses of 2.0 or 0.4 mg/kg/day for

6 months (route not specified), chlorpyrifos caused inhibition of plasma and red blood cell cholinesterase; at a dose of 0.08 mg/kg/day, only the plasma enzyme was inhibited in these animals [Hayes 1982]. Brain cholinesterase was not affected at any of these doses, and no clinical or morphological effects were noted at autopsy [Hayes 1982]. In 2-year feeding studies in dogs and rats, doses of 1 or 3 mg/kg/day produced depression of plasma and red blood cell cholinesterase; brain cholinesterase was depressed only at the highest dose [Hayes 1982]. In both rats and dogs, even the highest dose (3 mg/kg/day) produced no clinically important effects, as judged by survival, growth, relative and absolute organ weights, blood, urine, and clinical chemical findings, and gross and microscopic pathology [Hayes 1982]. In a three-generation reproduction and fertility study, no teratologic or reproductive effects were seen in male and female rats fed 1 mg/kg/day chlorpyrifos [ACGIH 1991].

2. *Effects on Humans:* In humans, chlorpyrifos is an inhibitor of plasma cholinesterase. The lowest toxic dose in humans is estimated to be 300 mg/kg; this dose caused peripheral nervous system effects, muscular weakness, and coma [NIOSH 1990]. Four repeated chlorpyrifos doses (10 mg/kg each) were applied to the skin of volunteers for a 24-hr period (each application) and caused no plasma cholinesterase depression; however, increasing the dose to 25 mg/kg did produce plasma cholinesterase inhibition, even when the duration of skin contact was reduced to 12 hr [ACGIH 1991]. Human male volunteers given 0.014 or 0.03-mg/kg chlorpyrifos per day for 20 days, followed by 0.1 mg/kg/day for an additional 9 days, showed no adverse behavioral effects or changes in hematology, urinalysis, or biochemistry parameters [Hayes 1982]. At the highest dose, plasma cholinesterase was depressed in these volunteers, but cholinesterase levels returned to normal within 4 weeks of the cessation of exposure. Red blood cell cholinesterase activity was not affected at any level [Hayes 1982]. Five of seven workers applying chlorpyrifos spray with hand-operated power sprayers (0.5% emulsion or 0.25% or 0.5% suspensions of water-wettable powder) had plasma cholinesterase values that were more than 50% below baseline values within 2 weeks after beginning work, and one worker had a plasma enzyme reduction that was greater than 70%. No inhibition of red blood cell cholinesterase was observed in these workers, and there were no signs or symptoms of illness [Hayes 1982; ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to chlorpyrifos depends on the route and extent of exposure. Inhalation can cause respiratory and ocular effects, often within a few minutes of exposure, and may cause a feeling of tightness in the chest, wheezing, laryngeal spasms, excessive salivation, bluish/purplish discoloration of the skin and lips, narrowed pupils, blurred vision, tearing, runny nose, or frontal headache. Ingestion of chlorpyrifos may cause anorexia, nausea, vomiting, abdominal cramps, and diarrhea. Skin absorption may result in localized sweating and muscle tremors in the area where skin absorption took place.

2. *Chronic exposure:* Repeated exposure to concentrations of chlorpyrifos too low to cause signs or symptoms after a single exposure may produce the signs and symptoms of poisoning described above. Continued daily exposure to low doses of chlorpyrifos may cause increasingly severe effects.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

If the victim is not breathing, clean any chemical con-

tamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chlorpyrifos or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorpyrifos and may result in worker exposures to this substance:

—Manufacture, formulation, and application of pesticides containing chlorpyrifos

—Use as an acaricide

—Use as an agricultural insecticide on corn, deciduous fruits and nuts, alfalfa, cotton, sorghum, and citrus crops and as a nonagricultural pesticide for household pests and aquatic larvae

—Use in controlling chinch bugs in Gulf Coast states and in controlling ticks on cattle and sheep in Australia

The following methods are effective in controlling worker exposures to chlorpyrifos, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chlorpyrifos, a licensed health care professional should evaluate and document the worker's base-

line health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood (plasma and red blood cell cholinesterase levels).

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorpyrifos at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the blood. Pre-exposure baseline plasma and red blood cell cholinesterase levels should be established.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorpyrifos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorpyrifos on plasma or red blood cell cholinesterase activity levels. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as chlorpyrifos. RBC ChE is an indicator of both acute and chronic overexposure. The recommended biological exposure index for chlorpyrifos (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for preexposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorpyrifos is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.05 and is found in OSHA Method No. 62 in the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If chlorpyrifos contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with chlorpyrifos should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chlorpyrifos, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles chlorpyrifos should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorpyrifos or a solution containing chlorpyrifos is handled, processed, or stored.

STORAGE

Chlorpyrifos should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accor-

dance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chlorpyrifos should be protected from physical damage and should be stored separately from strong acids (such as hydrochloric, sulfuric, or nitric acid), heat, sparks, and open flame. Because containers that formerly contained chlorpyrifos may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorpyrifos, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Use water spray to reduce vapors.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the chlorpyrifos for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Chlorpyrifos is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for chlorpyrifos is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorpyrifos emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chlorpyrifos is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation,

EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorpyrifos exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should only use respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with chlorpyrifos. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chlorpyrifos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated good resistance: laminates of Viton and neoprene or of butyl rubber and neoprene. Since specific test data are not available for chlorpyrifos, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chlorpyrifos.

If chlorpyrifos is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chlorpyrifos might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chlorpyrifos. Contact lenses should not be worn if the potential exists for chlorpyrifos exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROSTYRENE

INTRODUCTION

This guideline summarizes pertinent information about o-chlorostyrene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_8H_7Cl

- **Structure**

  $ClC_6H_4CH{=}CH$

- **Synonyms**

  2-Chlorostyrene; ortho-chlorostyrene

- **Identifiers**

  1. CAS No.: 2039-87-4
  2. RTECS No.: WL4160000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  o-Chlorostyrene is a combustible liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 138.6
  2. Boiling point (760 mm Hg): 188.7°C (371.7°F)
  3. Specific gravity (water = 1): 1.10 at 20°C (68°F)
  4. Vapor density: Data not available
  5. Melting point: -63.15°C (-81.67°F)
  6. Vapor pressure at 25°C (77°F): 0.096 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol, ether, acetone, petroleum ether, and acetic acid.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame
  2. Incompatibilities: None reported
  3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine) may be released in a fire involving o-chlorostyrene.
  4. Special precautions: None reported

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- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for o-chlorostyrene; however, other sources report that this substance is combustible.

1. Flash point: 58.9°C (138°F)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or foam

Fires involving o-chlorostyrene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorostyrene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for o-chlorostyrene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 50 ppm (285 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 75 ppm (430 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-chlorostyrene a threshold limit value (TLV) of 50 ppm (283 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 75 ppm (425 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The ACGIH limits are based on the risk of liver, kidney, and narcotic effects associated with exposure to o-chlorostyrene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorostyrene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, o-chlorostyrene is toxic to the liver and kidneys. Applied to rabbit skin for 24 hr, 10 mg of o-chlorostyrene caused irritation [Sax and Lewis 1989]. The dermal LD_{50} in rabbits is 20 g/kg [Sax and Lewis 1989]. The instillation of 500 mg into the eyes of rabbits also caused irritation [Sax and Lewis 1989]. The oral LD_{50} in rats is 5.2 g/kg [Sax and Lewis 1989]. A group of 24 rats, 3 rabbits, 12 guinea pigs, and 1 dog of each sex were exposed 7 hr/day, 5 days/week for a total of 130 exposures in 180 days to an analytically determined average o-chlorostyrene concentration of 101 ppm (576 mg/m^3). No adverse effects on appearance, growth, demeanor, mortality, hematology, or blood chemistry values were apparent; at autopsy, no changes in organ weights or gross pathology were evident. However, microscopic examination of the liver and kidney tissues of animals of all four species showed a slightly higher incidence than in controls of changes in these organs [ACGIH 1991].
2. *Effects on Humans:* No toxic effects of o-chlorostyrene exposure have been reported in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Based on effects seen in animals, contact of the skin or eyes with o-chlorostyrene may cause irritation.
2. *Chronic exposure:* Based on effects seen in animals, long-term exposure to o-chlorostyrene may cause hematuria, proteinuria, acidosis, an enlarged liver, jaundice, and elevated liver enzymes.

• **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of o-chlorostyrene. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorostyrene or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorostyrene and may result in worker exposures to this substance:

—Use in organic synthesis and in the preparation of specialty polymers

The following methods are effective in controlling worker exposures to o-chlorostyrene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveil-

lance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to o-chlorostyrene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and kidneys.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorostyrene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the liver or kidneys.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorostyrene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorostyrene on the liver or kidneys. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-chlorostyrene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorostyrene is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). STEL and TWA samples are both collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 20 liters (TWA) or 3 liters (STEL) is collected. The sample is then treated with carbon disulfide to extract the o-chlorostyrene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If o-chlorostyrene contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with o-chlorostyrene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of o-chlorostyrene.

A worker who handles o-chlorostyrene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where o-chlorostyrene or a solution containing o-chlorostyrene is handled, processed, or stored.

STORAGE

o-Chlorostyrene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorostyrene should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained o-chlorostyrene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorostyrene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
6. For large liquid spills, call the local fire department.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorostyrene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-chlorostyrene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorostyrene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorostyrene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of

o-chlorostyrene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with o-chlorostyrene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-chlorostyrene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-chlorostyrene.

If o-chlorostyrene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorostyrene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorostyrene. Contact lenses should not be worn if the potential exists for o-chlorostyrene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-CHLORO-6-TRICHLOROMETHYL PYRIDINE

INTRODUCTION

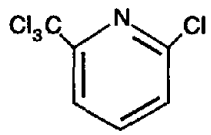
This guideline summarizes pertinent information about 2-chloro-6-trichloromethyl pyridine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_3Cl_4N$

- **Structure**



- **Synonyms**

Nitrapyrin; α,α,α-6-tetrachloro-2-picoline; N-Serve, N-Serve nitrogen stabilizer; Dowco-163

- **Identifiers:**

1. CAS No.: 1929-82-4
2. RTECS No.: US7525000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

2-Chloro-6-trichloromethyl pyridine is a colorless or white, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 230.93
2. Boiling point (11 mm Hg): 136°–137.5°C (276.8°–279.5°F)
3. Specific gravity (water = 1): Data not available
4. Vapor density: Not applicable
5. Melting point: 62.5°–62.9°C (144.5°–145.2°F)
6. Vapor pressure: 0.0028 mm Hg at 23°C (73.4°F)
7. Solubility: Insoluble in water
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Aluminum, magnesium, or their alloys

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3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving 2-chloro-6-trichloromethyl pyridine.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for 2-chloro-6-trichloromethyl pyridine.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving boron oxide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2-chloro-6-trichloromethyl pyridine.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for 2-chloro-6-trichloromethyl pyridine are 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limits (RELs) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 20 mg/m^3. The STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-chloro-6-trichloromethyl pyridine a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 20 mg/m^3 for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 min [ACGIH 1991].

- **Rationale for limits**

The OSHA limits are based on the risk of physical irritation associated with exposure to 2-chloro-6-trichloromethyl pyridine [54 Fed. Reg. 2592 (1989)].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2-chloro-6-trichloromethyl pyridine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, 2-chloro-6-trichloromethyl pyridine is moderately toxic when ingested or absorbed through the skin. The dermal LD_{50} in rabbits is 850 mg/kg [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50}s in rats, mice, and rabbits are 940 mg/kg, 710 mg/kg, and 500 mg/kg respectively [NIOSH 1993; Sax and Lewis 1989]. Dogs and rats fed 15 mg/kg 2-chloro-6-trichloromethyl pyridine daily for 93 days showed no adverse effects on behavior, growth, food consumption, body and organ weights, mortality, or serum chemistries; at autopsy, no gross or microscopic changes to the organs or tissues were detectable [ACGIH 1991]. Male rats fed concentrations of 1,000 ppm in the diet for 2 years had a statistically significant reduction in mean body weight at 12 months, but not at 18 and 24 months. No effects were recorded at lower concentrations. Female rats fed between 30 and 1,000 ppm for 2 years had an increased incidence of bile duct hyperplasia [Dow Chemical USA 1967].

2, *Effects on Humans:* There are no data on the acute or chronic effects of exposure to 2-chloro-6-trichloromethyl pyridine in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to 2chloro-6-trichloromethyl pyridine may irritate the eyes, nose, throat, and skin. Higher levels may cause dizziness and lightheadness.

2. *Chronic exposure:* Chronic exposure to 2-chloro-6-trichloromethyl pyridine may cause dizziness, headaches, loss of appetite and insomnia. Repeated exposure may affect the liver and kidneys.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2-chloro-6-trichloromethyl pyridine or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 2-chloro-6-trichloromethyl pyridine and result in worker exposures to this substance:

—Use as a fertilizer additive to control nitrification and prevent loss of soil nitrogen from land to be planted with corn, cotton, wheat, or sorghum

—Manufacture, formulation, and application of 2-chloro-6-trichloromethyl pyridine-containing products

Methods that are effective in controlling worker exposures to 2-chloro-6-trichloromethyl pyridine, depending on the feasibility of implementation, are:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH:

American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-chloro-6-trichloromethyl pyridine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the kidneys, liver, eyes, and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-chloro-6-trichloromethyl pyridine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) including a history and other findings consistent with diseases of the kidneys, liver, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-chloro-6-trichloromethyl pyridine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-chloro-6-trichloromethyl pyridine on the kidneys, liver, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-chloro-6-trichloromethyl pyridine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

The OSHA method for determining worker exposure to airborne concentrations of 2-chloro-6-trichloromethyl

pyridine (total dust) is made using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Particulates not otherwise regulated (Total Dust) [OSHA 1987].

The OSHA method for determining worker exposure to airborne concentrations of 2-chloro-6-trichloromethyl pyridine (respirable fraction) is made using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is preceded by a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Particulates not otherwise regulated (Respirable Fraction) [OSHA 1987].

PERSONAL HYGIENE

If 2-chloro-6-trichloromethyl pyridine contacts the skin, workers should wash the skin with soap and water.

Clothing contaminated with 2-chloro-6-trichloromethyl pyridine should be removed.

A worker who handles 2-chloro-6-trichloromethyl pyridine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or apply cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2-chloro-6-trichloromethyl pyridine or a solution containing 2-chloro-6-trichloromethyl pyridine is handled, processed, or stored.

STORAGE

2-Chloro-6-trichloromethyl pyridine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. This substance should not be stored in unlined containers or be pumped with equipment made of aluminum, magnesium, or alloys of these metals. Containers of 2-chloro-6-trichloromethyl pyridine should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-chloro-6-trichloromethyl pyridine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. No specific information is available on clean-up procedures for spills or leaks involving this substance.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  2-Chloro-6-trichloromethyl pyridine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the National Response Center of an accidental release of 2-chloro-6-trichloromethyl pyridine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of 2-chloro-6-trichloromethyl pyridine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-

261.24. Although 2-chloro-6-trichloromethyl pyridine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-chloro-6-trichloromethyl pyridine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with 2-chloro-6trichloromethyl pyridine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-chloro-6-trichloromethyl pyridine. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-chloro-6-trichloromethyl pyridine.

If 2-chloro-6-trichloromethyl pyridine is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-chloro-6-trichloromethyl pyridine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-chloro-6-trichloromethyl pyridine. Contact lenses should not be worn if the potential exists for 2-chloro-6-trichloromethyl pryidine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROTOLUENE

INTRODUCTION

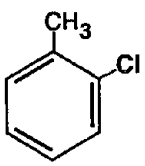
This guideline summarizes pertinent information about o-chlorotoluene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CH_3C_6H_4Cl$

- **Structure**



- **Synonyms**

2-Chloro-1-methylbenzene; 2-chlorotoluene; 2-methylchlorobenzene; 1-methyl-2-chlorobenzene; *o*-tolyl chloride; Halso 99

- **Identifiers**

1. CAS No.: 95-49-8
2. RTECS No.: XS9000000
3. DOT UN: 2238 27
4. DOT label: Flammable liquid

- **Appearance and odor**

o-Chlorotoluene is a colorless liquid. The odor threshold for o-chlorotoluene is 0.32 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 126.59
2. Boiling point (760 mm Hg): 159°C (318.2°F)
3. Specific gravity (water = 1): 1.083 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-chlorotoluene): 4.37
5. Melting point: -35.1°C (-31.18°F)
6. Vapor pressure at 43.2°C (109.8°F): 10 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; freely soluble in alcohol, acetone, ether, benzene, carbon tetrachloride, and chloroform

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of o-chlorotoluene with oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving o-chlorotoluene.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to o-chlorotoluene (unspecified isomer, mixture, or concentration).

1. Flash point: 52°C (126°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, CO_2, water spray, or standard foam to fight fires involving o-chlorotoluene.

Fires involving o-chlorotoluene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of o-chlorotoluene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorotoluene. Structural firefighters' protective clothing may provide limited protection against fires involving o-chlorotoluene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for o-chlorotoluene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) as 50 ppm (250 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 75 ppm (375 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-chlorotoluene a threshold limit value (TLV) of 50 ppm (259 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of moderate skin and eye irritation. The ACGIH limit is based on the risk of eye and skin irritation and systemic poisoning associated with exposure to o-chlorotoluene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorotoluene can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, o-chlorotoluene is irritating to the eyes and skin and, at high doses, this substance affects the central nervous system. A 24-hr patch test with o-chlorotoluene showed moderate skin irritation on both abraded and intact rabbit skin [ACGIH 1991]. Undiluted liquid o-chlorotoluene applied to the skin of guinea pigs under an occlusive dressing in doses of 1 ml/kg or 10 ml/kg for a 24-hr period caused moderately severe local irritation and evidence of skin absorption [ACGIH 1991]. One drop of undiluted o-chlorotoluene instilled into the eye of a rabbit resulted in moderate conjunctival erythema; the cornea was opaque 24 hr after instillation but appeared normal 2 weeks later [ACGIH 1991]. The oral LD_{50} in rats is 5,700 mg/kg, and three of 20 rats died after inhaling approximately 2,400 ppm [EPA 1989]. Rats exposed by inhalation for 6 hr to a 4,000-ppm concentration of o-chlorotoluene lost coordination in 1.5 hr, became prostrate after 1.75 hr, and showed tremors after 2 hr of exposure; marked vasodilation also developed in these animals. All three rats survived, however, and had gained weight (averaging 33 grams) 2 weeks later. Mice, rats, and guinea pigs exposed at a chamber concentration of 4,400 ppm exhibited the following: gasping, ataxia, and convulsions in mice within 30 min after exposure, and gasping, hyperpnea, ataxia, and convulsions in rats and guinea pigs in 45 min. All animals were comatose in 60 min. All mice and rats died as did 7 of 10 guinea pigs. Two guinea pigs were alive 2 week postexposure [ACGIH 1991]. Three rats exposed to 14,000 ppm o-chlorotoluene survived but showed loss of coordination, vasodilation, labored respiration, and narcosis. Of three rats exposed to 175,000 ppm, two were severely incapacitated while the other died. The two that survived were gaining weight 2 weeks later [ACGIH 1991].

2. *Effects on Humans:* There are no reports of the effects of exposure to o-chlorotoluene in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Based on effects seen in animals, acute overexposure to o-chlorotoluene may cause dizziness; loss of coordination; tremors; difficult breathing; redness, inflammation, and tearing of the eyes; and redness and inflammation of the skin.

2. *Chronic exposure:* No signs or symptoms of continued low-level exposure to o-chlorotoluene have been reported.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of o-chlorotoluene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorotoluene or any material containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorotoluene and may result in worker exposures to this substance:

—Use as a solvent and as an intermediate in the production of organic chemicals, pharmaceuticals, synthetic rubber compounds, and dyes

—Use as an intermediate in the production of herbicides

The following methods are effective in controlling worker exposures to o-chlorotoluene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

— Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

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Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to o-chlorotoluene, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and central nervous system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorotoluene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorotoluene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorotoluene on the eyes, skin, or central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-chlorotoluene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorotoluene is determined by using a charcoal tube (100/150-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 20 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is an OSHA modification of NIOSH Method 1003, *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If o-chlorotoluene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with o-chlorotoluene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of o-chlorotoluene, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles o-chlorotoluene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where o-chlorotoluene is handled, processed, or stored.

STORAGE

o-Chlorotoluene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorotoluene should be protected from physical damage and should be stored separately from oxidizing materials, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained o-chlorotoluene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorotoluene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and gently place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the o-chlorotoluene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorotoluene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR Part 355.40] to notify the National Response Center of an accidental release of o-chlorotoluene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorotoluene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorotoluene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-chlorotoluene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves and other protective clothing, as appropriate) should be worn to prevent any skin contact with o-chlorotoluene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Viton® may withstand permeation by o-chlorotoluene for more than 4 but fewer than 8 hr. The following materials have breakthrough times of less than 1 hr and are not recommended for use with o-chlorotoluene: butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Saranex.

If o-chlorotoluene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorotoluene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorotoluene.

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ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

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NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CLOPIDOL

INTRODUCTION

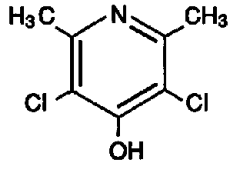
This guideline summarizes pertinent information about clopidol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_7H_7Cl_2NO$

- **Structure**



- **Synonyms**

  3,5-Dichloro-2,6-dimethyl-4-pyridinol; methylchloropindol; clopindol; Farmcoccid; Coccidiostat C; Coyden; Lerbek

- **Identifiers**

  1. CAS No.: 2971-90-6
  2. RTECS No.: UU7711500
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Clopidol is a white to light brown crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 192.06
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: Greater than 320°C (608°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water

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8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat. In cloud form, clopidol dust may explode if ignited.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving clopidol.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to clopidol; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving clopidol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving clopidol.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for clopidol is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek and 20 mg/m^3 as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure which should not be exceeded at any time during the workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned clopidol a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to clopidol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to clopidol can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Clopidol is an antibiotic used in veterinary medicine as a coccidiostat in poultry. This substance has a low order of acute and chronic toxicity in experimental animals [ACGIH 1991]. The oral LD_{50} in rabbits and guinea pigs is greater than 8 g/kg [NIOSH 1993]. The oral LD_{50} in rats is 18 g/kg [NIOSH 1993; Merck 1983]. Rats fed 15 mg/kg clopidol daily for 2 years showed no adverse effects [ACGIH 1991]. Dogs fed 5 mg/kg clopidol daily (duration of experiment not specified) also showed no adverse effects [ACGIH 1991].

2. *Effects on Humans:* In humans, exposure to clopidol dust may cause physical irritation of the eyes, nose, throat, and skin [NJDH 1986]. No chronic effects have been reported [NJDH 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to clopidol may cause redness and itching of the eyes, runny nose, sore throat, coughing, and redness and irritation of the skin.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to clopidol have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of clopidol is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve clopidol and may result in worker exposures to this substance:

—Manufacture and formulation of this substance

—Use as a coccidiostat in poultry

The following methods are effective in controlling worker exposures to clopidol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to toxic substances should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of

adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to clopidol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to clopidol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to clopidol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of clopidol on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for clopidol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne clopidol is determined by using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected (total dust) or with a 10-mm nylon cyclone preceding the glass fiber filter at a flow rate of 1.7 liter/min until a recommended air volume of 204 liters is collected (respirable fraction). Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If clopidol collects on the skin in excessive amounts, workers should wash the affected areas with soap and water.

Clothing excessively contaminated with clopidol should be removed to avoid local irritation of the skin.

A worker who handles clopidol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or

apply cosmetics in areas where clopidol or a solution containing clopidol is handled, processed, or stored.

STORAGE

Clopidol should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of clopidol should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving clopidol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or disposal.
4. Absorb liquid clopidol-containing formulations in vermiculite, dry sand, earth, or similar material.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Clopidol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of clopidol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of clopidol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although clopidol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of clopidol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use

only those respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent excessive skin contact with clopidol. Safety glasses, goggles, or face shields should be worn during operations in which clopidol might contact the eyes.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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NIOSH [1993]. Registry of toxic effects of chemical substances database: clopidol. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

NJDH [1986]. Hazardous Substance Fact Sheet. Clopidol. Trenton, NJ: New Jersey Department of Health.

OSHA [1989]. OSHA laboratory in-house methods file. Salt Lake City, UT: U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COBALT CARBONYL

INTRODUCTION

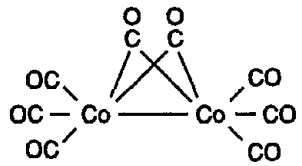
This guideline summarizes pertinent information about cobalt carbonyl (measured as Co) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8Co_2O_8$

- **Structure**



- **Synonyms**

Cobalt octacarbonyl, cobalt tetracarbonyl, cobalt tetracarbonyl dimer, di-μ-carbonylhexacarbonyl-dicobalt, dicobalt carbonyl, dicobalt octacarbonyl, octacarbonyldicobalt

- **Identifiers**

1. CAS No.: 10210-68-1
2. RTECS No.: GG0300000
3. DOT UN: 9188 31 (Hazardous substance, liquid, or solid, n.o.s.)
4. DOT label: None

- **Appearance and odor**

Cobalt carbonyl is an orange to dark brown crystalline solid, although the pure substance is white.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 341.94
2. Boiling point (at 760 mm Hg): Decomposes at temperatures above 52°C (125.6°F)
3. Specific gravity (water = 1): 1.87 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 51°C (123.8°F)
6. Vapor pressure at 15°C (59°F): 0.07 mm Hg
7. Solubility: Insoluble in water; soluble in alcohol, ether, naphtha, and carbon disulfide
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Exposure of cobalt carbonyl to air or heat causes decomposition to occur. Cobalt carbonyl is slowly attacked by sulfuric

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Occupational Safety and Health Administration

acid or hydrochloric acid and is more rapidly attacked by bromine and nitric acid.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) and the pyrophoric dodecacarbonyltetracobalt may be released in a fire involving cobalt carbonyl.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to cobalt carbonyl.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Data not available

4. Extinguishant: For small fires involving cobalt carbonyl, use dry chemical, carbon dioxide, water spray, or standard foam. For large fires, use water spray, fog, or standard foam.

Fires involving cobalt carbonyl should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Containers of cobalt carbonyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Do not scatter this material with high-pressure water streams. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cobalt carbonyl. Structural firefighters' protective clothing may provide limited protection against fires involving this substance.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cobalt carbonyl (measured as Co) [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cobalt carbonyl (measured as Co) a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation. The ACGIH limit is based on the risk of pulmonary and other acute effects associated with exposure to cobalt carbonyl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cobalt carbonyl can occur through inhalation, ingestion, and contact with the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cobalt carbonyl damages the respiratory and central nervous systems, liver, and kidneys, and may also irritate and sensitize the skin of animals on contact. Administered topically or subcutaneously to rats and mice, cobalt carbonyl was absorbed through the skin in toxic amounts and caused irritation of the skin [NLM 1990]. Applied to the skin of guinea pigs, cobalt carbonyl caused an allergic reaction [NLM 1990]. The LC_{50} (duration unspecified) in rats is 165 mg/m^3 [NIOSH 1989] and the 2-hr LC_{50} in mice is 27 mg/m^3 [Sax and Lewis 1989]. Rats exposed to concentrations of cobalt carbonyl ranging from 8 to 44 mg/m^3 for 30 min showed inflammatory and proliferative changes in the lungs at autopsy; at the highest concentrations, there was evidence of pulmonary edema. Histopathological changes and adverse effects on the central nervous system, liver, and kidneys were seen at autopsy; decreased thyroid function was also observed in these animals [NLM 1990]. The oral LD_{50} is 754 mg/kg in

rats [NIOSH 1989] and 378 mg/kg in mice [Sax and Lewis 1989].

2. *Effects on Humans:* Cobalt carbonyl causes sensory irritation on contact with the skin and mucous membranes [Parmeggiani 1983], and affects the respiratory system and the blood. Factory workers acutely overexposed to airborne cobalt carbonyl developed bronchospasm, showed X-ray evidence of focal infiltrations of the lungs, and had changes in several cellular blood components [NLM 1990]. Based on the toxicologic similarities between nickel carbonyl and cobalt carbonyl, it is likely that overexposure to cobalt carbonyl would give rise to nausea, headache, dizziness, coughing, dyspnea, and substernal pain [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cobalt carbonyl may cause cough, shortness of breath, lung densities, decreased pulmonary function, wheezing, and pain in the chest. Clinical evidence of changes in the cellular components of the blood may also be present. Ingestion could cause pericardial effusion, pain, vomiting, nerve deafness, convulsions, and thyroid enlargement.

2. *Chronic exposure:* Continued low-level exposure to cobalt carbonyl may cause cough, rapid breathing on exertion, decreased pulmonary function, wheezing, and shortness of breath.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove all contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cobalt carbonyl or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do not give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cobalt carbonyl and result in worker exposures to this substance:

—Use as a catalyst for organic reactions

—Use as a catalyst in the plastics industry

—Preparation of metals of high purity

The following methods are effective in controlling worker exposures to cobalt carbonyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cobalt carbonyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory and nervous systems, liver, kidneys, and blood. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cobalt carbonyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory or nervous system, liver, kidneys, or blood.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cobalt carbonyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cobalt carbonyl on the respiratory or nervous system, liver, kidneys, or blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cobalt carbonyl.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to cobalt carbonyl may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cobalt carbonyl (measured as cobalt) is determined by using a 0.8 micron mixed cellulose ester filter. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Computerized Information System [OSHA 1990], the *OSHA Analytical Methods Manual* [OSHA 1985], the *OSHA Chemical Information Manual* [OSHA 1987], and in Method 7027 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If cobalt carbonyl contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min, and then wash with soap and water.

Clothing contaminated with cobalt carbonyl should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cobalt carbonyl, particularly its potential to cause headache, nausea, and pulmonary effects.

A worker who handles cobalt carbonyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cobalt carbonyl or a solution containing this substance is handled, processed, or stored.

STORAGE

Cobalt carbonyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of cobalt carbonyl should be protected from physical damage and should be stored separately from hydrochloric acid, sulfuric acid, nitric acid, bromine, heat, sparks, and open flame. Because containers that formerly contained cobalt carbonyl may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving cobalt carbonyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Cover the spill area with a plastic sheet or tarp to minimize spreading.

2. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of cobalt carbonyl must comply with EPA's emergency planning requirements [40 CFR Part 355.30]. (If cobalt carbonyl is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 10 lb or more of cobalt carbonyl are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, dis-

charging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for cobalt carbonyl is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cobalt carbonyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cobalt carbonyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cobalt carbonyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with cobalt carbonyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cobalt carbonyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cobalt carbonyl.

If cobalt carbonyl is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cobalt carbonyl might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cobalt carbonyl. Contact lenses should not be worn if the potential exists for cobalt carbonyl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COBALT HYDROCARBONYL

INTRODUCTION

This guideline summarizes pertinent information about cobalt hydrocarbonyl (measured as cobalt) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $HCo(CO)_4$

- **Synonyms**

  Tetracarbonylhydrocobalt; hydridotetracarbonyl cobalt; hydrocobalt tetracarbonyl; tetracarbonylhydridocobalt

- **Identifiers**

  1. CAS No.: 16842-03-8
  2. RTECS No.: GG0900000
  3. DOT UN: 1954 22 (Flammable gas, n.o.s.)
  4. DOT label: Flammable gas

- **Appearance and odor**

  Cobalt hydrocarbonyl is a flammable gas that is unstable and decomposes rapidly at room temperature.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 171.98
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity: Data not available
  4. Relative gas density: 5.93
  5. Freezing point: -26.2°C (-15.2°F)
  6. Vapor pressure at 20°C (68°F): >1 atm
  7. Solubility: Sparingly soluble in water
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Contact of cobalt hydrocarbonyl with air causes decomposition.
  2. Incompatibilities: None reported
  3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving cobalt hydrocarbonyl.
  4. Special precautions: None reported

- **Flammability**

  The National Fire Protection Association has not assigned a flammability rating for cobalt hydrocarbonyl; however, this substance is flammable.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Flash point: Not applicable (Flammable gas)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical or carbon dioxide for small fires and water spray or fog for large fires.

Fires involving cobalt hydrocarbonyl should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cobalt hydrocarbonyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions, and let the tank car or truck burn unless the leak can be stopped. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cobalt hydrocarbonyl. Structural firefighters' protective clothing will provide limited protection.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cobalt hydrocarbonyl [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cobalt hydrocarbonyl a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation associated with exposure to cobalt hydrocarbonyl. The ACGIH limit is based on the risk of lung, liver, and kidney effects associated with exposure to cobalt hydrocarbonyl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cobalt hydrocarbonyl can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cobalt hydrocarbonyl affects the respiratory system. The 2-hr LC_{50} for cobalt hydrocarbonyl is 46.2 mg/m^3 in rats and 17.5 mg/m^3 in mice [NIOSH 1993]. Acutely poisoned animals showed signs of chemical pneumonitis before death [Palmer et al. 1959]. Dogs, rats, and guinea pigs exposed 6-hr/day on 71 occasions within a 3-month period to cobalt hydrocarbonyl decomposition products at an average cobalt concentration of 9 mg/m^3 showed elevated hemoglobin levels (rats) and foam cell aggregates in the lungs; these signs disappeared after the cessation of exposure [Palmer et al. 1959].

2. *Effects on Humans:* No adverse effects of exposure to cobalt hydrocarbonyl have been reported in humans.

- **Signs and symptoms of exposure**

1. *Acute or sub-chronic exposure:* Based on effects seen in animals, subchronic exposure to cobalt hydrocarbonyl may cause difficult breathing, coughing, reduced lung function, and fluid in the lungs.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to cobalt hydrocarbonyl have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cobalt hydrocarbonyl and may result in worker exposures to this substance:

—Manufacture of cobalt hydrocarbonyl

—Use as a catalyst

The following are methods that are effective in controlling worker exposures to cobalt hydrocarbonyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cobalt hydrocarbonyl, the licensed health

care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cobalt hydrocarbonyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cobalt hydrocarbonyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cobalt hydrocarbonyl on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cobalt hydrocarbonyl.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cobalt hydrocarbonyl (measured as cobalt) is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a recommended flow rate of 2.0 liters/min until a recommended air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy for total cobalt. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cobalt hydrocarbonyl contacts the skin, the victim should immediately and thoroughly wash the affected areas with soap and water.

Clothing contaminated with cobalt should be removed immediately.

A worker who is exposed to cobalt hydrocarbonyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cobalt hydrocarbonyl is generated.

STORAGE

Cobalt hydrocarbonyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of cobalt hydrocarbonyl should be protected from physical damage and should be stored separately from air, heat, sparks, and open flame.

LEAKS

In the event of a leak involving cobalt hydrocarbonyl, persons not wearing protective equipment and clothing

should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate potentially explosive atmospheres.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cobalt hydrocarbonyl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cobalt hydrocarbonyl; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cobalt hydrocarbonyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cobalt hydrocarbonyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cobalt hydrocarbonyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowl-

edgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with cobalt hydrocarbonyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cobalt hydrocarbonyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cobalt hydrocarbonyl.

Safety glasses, goggles, or face shields should be worn during operations in which cobalt hydrocarbonyl might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cobalt hydrocarbonyl.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRUFOMATE

INTRODUCTION

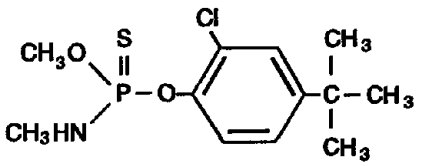
This guideline summarizes pertinent information about crufomate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{19}ClNO_3P$

- **Structure**



- **Synonyms**

Amidofos; 4-tert-butyl-2-chlorophenyl methyl methylphosphoramidate; Dowco 132; Montrel; o-methyl-o-2-chloro-4-tert-butylphenyl N-methylamidophosphate; Ruelene

- **Identifiers**

1. CAS No.: 299-86-5
2. RTECS No.: TB3850000
3. DOT UN: 2765 55 (phenoxy pesticides, solid, toxic, n.o.s.)
4. DOT label: Poison or St. Andrew's Cross (depending on quantity shipped)

- **Appearance and odor**

Crufomate is a white, crystalline solid in pure form; the commercial product is a yellow oil. Crufomate is an organophosphorus pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data

1. Molecular weight: 291.7
2. Boiling point (0.01 mm Hg): 117° to 118°C (242.6° to 244.4°F)
3. Specific gravity (water = 1): 1.2 at 70°C (158°F)
4. Vapor density: Not applicable
5. Melting point: 60° to 60.5°C (140° to 141°F) (pure); 58.7°C (137.7°F) (92%, technical grade)

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6. Vapor pressure at 117°C (242.6°F): 0.01 mm Hg

7. Solubility: Practically insoluble in water and light petroleum; soluble in benzene, alcohol, ethyl ether, cyclohexane, carbon tetrachloride, and acetonitrile.

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, open flame, strong alkalies, and strong acids. Crufomate is unstable over long periods of time, in water preparations, and at temperatures above 60°C (140°F).

2. Incompatibilities: Crufomate decomposes in strongly alkaline (greater than pH 7) and strongly acidic media.

3. Hazardous decomposition products: Toxic gases (such as oxides of phosphorus and nitrogen, and chlorine) may be released in a fire involving crufomate.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to crufomate.

1. Flash point: 41.1° to 60°C (106° to 140°F), depending on the formulation

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or standard foam for small fires. Water spray, fog, or standard foam is recommended to fight large fires involving crufomate.

Fires involving crufomate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of crufomate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving crufomate. Chemical protective clothing that is specifically recommended for crufomate may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving crufomate.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for crufomate [29 CFR 1910.1000, Table Z- 1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 20 mg/m^3 as a 15-min short-term exposure limit (STEL). A STEL is a 15-min TWA concentration that should not be exceeded at any time during a workday [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned crufomate a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of neurotoxicity and cholinesterase inhibition. The ACGIH limit is based on the risk of cholinesterase inhibition associated with exposure to crufomate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to crufomate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, crufomate is an inhibitor of plasma and erythrocyte cholinesterase.

Application of crufomate to the eye of rabbits as undiluted or 10% solutions resulted in corneal cloudiness and conjunctival irritation, along with slight pain [Clayton and Clayton 1982; ACGIH 1991]. Crufomate produced slight erythema when applied undiluted or as a 10% solution to the abraded or intact skin of the rabbit [Clayton and Clayton 1982; ACGIH 1991]. The dermal LD_{50} in rabbits is 2,000 mg/kg [NIOSH 1992b]. The lowest toxic inhalation dose in rats is 12 mg/m^3 for 4 hr [NIOSH 1992b]. The oral LD_{50} is 460 mg/kg in rats, 400 mg/kg in rabbits, and 1,000 mg/kg in guinea pigs [NIOSH 1992b]. Dogs fed 250 ppm crufomate in the diet for 75 days exhibited depression of blood cholinesterase and slight liver morphological changes; no effects were observed in dogs given dietary doses of 40 or 125 ppm [Clayton and Clayton 1982]. In 90-day dietary studies in rats, blood and/or brain cholinesterase levels were depressed 40% to 60% as compared with levels in untreated controls when doses of 30 to 1,000 ppm (1.5 to 50 mg/kg/day) were administered; no other adverse effects were observed in these animals [Clayton and Clayton 1982]. Rats fed 1,000 ppm (50 mg/kg/day) for 2 years showed marked cholinesterase inhibition, growth retardation, atrophy of the muscles of the hind limbs, and slight degeneration of the sciatic nerve; after 12, 18, or 24 months on this regimen, there was a 50% reduction in testes weights, reflecting degeneration and atrophy of the seminiferous tubules [Clayton and Clayton 1982]. No teratologic or reproductive effects were seen in male and female rats fed up to 500 ppm crufomate (25 mg/kg/day) for three generations [Clayton and Clayton 1982]. In female mice treated dermally with 50 or 100 mg/kg crufomate on days 35 and 21 before mating, the lower dose prolonged the gestation period and decreased the index of lactation and the higher dose reduced conception rate, litter size, and lactation index and decreased fetal body weight [NLM 1992].

2. *Effects on Humans:* In humans, crufomate is a moderately potent cholinesterase inhibitor.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute overexposure to crufomate by the oral route may cause severe gastrointestinal effects such as cramps, diarrhea, nausea, and anorexia. Acute inhalation exposure can cause wheezing, difficult breathing, blurred vision, and tearing. Dermal exposure causes localized twitching and sweating. Severe overexposure by any route can cause respiratory paralysis, coma, and death.

2. *Chronic exposure:* Continued low-level exposure to crufomate may lead to acetylcholine buildup, causing the signs and symptoms of systemic poisoning described above for acute overexposure.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air immediately. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if crufomate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve crufomate and may result in worker exposures to this substance:

—Manufacture of crufomate and crufomate-containing pesticides

—Formulation and application of crufomate and crufomate-containing pesticides

—Use as a selective insecticide against cattle grubs, horn flies, and lice

The following methods are effective in controlling worker exposures to crufomate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to crufomate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood. A pre-exposure plasma and red blood cell cholinesterase activity baseline should also be established.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to crufomate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration

of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma and red blood cell cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to crufomate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of crufomate on the levels of plasma or red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Absorption of crufomate can be confirmed by analysis of urine for its metabolite, crufomate phenol. However, correlations between airborne and urinary levels of crufomate and its metabolite have not been established. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as crufomate. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for crufomate (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne crufomate is determined by using an OSHA Versatile Sampler (OVS-2) with a 13 mm XAD-2 tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method is described in OSHA's Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If crufomate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with crufomate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of crufomate.

A worker who handles crufomate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where crufomate or a solution containing crufomate is handled, processed, or stored.

STORAGE

Crufomate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Crufomate is unstable over long periods of time in water preparations and at temperatures above 60°C (140°F). Containers of crufomate must be stacked in a manner that permits free circulation of air below and inside the pile of containers. Containers of crufomate should be protected from physical damage and should be stored separately from strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained crufomate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving crufomate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Water spray may be used to reduce vapors.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the crufomate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Crufomate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of crufomate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of crufomate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although crufomate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of crufomate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory pro-

tection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with crufomate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to crufomate permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated some resistance to permeation by these compounds: a laminate of Viton and neoprene, or a laminate of butyl rubber and neoprene. Since specific test data are not available for crufomate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to crufomate.

If crufomate is dissolved an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which crufomate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with crufomate.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYANOGEN

INTRODUCTION

This guideline summarizes pertinent information about cyanogen for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $(CN)_2$

- **Synonyms**

  Carbon nitride, dicyan, dicyanogen, ethane dinitrile, nitriloacetonitrile, oxalic acid dinitrile, oxalic nitrile, oxalonitrile, oxalyl cyanide, prussite

- Identifiers

  1. CAS No.: 460-19-5
  2. RTECS No.: GT1925000
  3. DOT UN: 1026 18
  4. DOT label: Poison Gas; Flammable Gas

- **Appearance and odor**

  Cyanogen is a highly flammable, colorless gas with a pungent, penetrating, almond-like odor; this substance is shipped as a liquefied gas under its own vapor pressure. The odor threshold is reported to be 250 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 52.04
  2. Boiling point (760 mm Hg): -21.17°C (-6.1°F)
  3. Specific gravity (for the liquid) (water = 1): 0.95 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyanogen): 1.8
  5. Melting point: -27.9°C (-18.2°F)
  6. Vapor pressure at 21°C (69.9°F): 3,868.4 mm Hg
  7. Solubility: Soluble in water, alcohol, and ether
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, shock, and direct sunlight

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2. Incompatibilities: Contact of cyanogen with acids or their vapors, water, liquid oxygen, or oxidizers (such as chlorine, fluorine, or bromine) causes explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as cyanide, hydrogen cyanide, carbon monoxide, and oxides of nitrogen) may be released in a fire involving cyanogen.

4. Special precautions: Cyanogen is denser than air and can collect in enclosed spaces. It can flow along the surface, reach distant, low-lying sources of ignition, and flash back.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to cyanogen.

1. Flash point: Cyanogen has a wide range of explosiveness.

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 6.6; upper, 32

4. Extinguishant: Let the fire burn unless the leak can be stopped immediately. Use water spray, fog, or standard foam to fight large fires involving cyanogen. Water may be used to cool fire-exposed containers and to protect persons attempting to stop the leak.

Fires involving cyanogen should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Cyanogen is heavier than air and may travel to a source of ignition and flash back. Containers of cyanogen may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyanogen. Chemical protective clothing that is specifically recommended for cyanogen may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing may provide limited protection against fires involving cyanogen.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyanogen [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (20 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyanogen a threshold limit value (TLV) of 10 ppm (21 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and respiratory irritation associated with cyanogen exposure. The ACGIH limit is based on the risk of irritant and systemic effects associated with exposure to cyanogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyanogen can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Cyanogen is a highly toxic gas that causes severe irritation, respiratory distress, and death on acute exposure. Rabbits survived dermal exposure to 10,000 ppm for 8 hours without apparent systemic effects [McNerney and Schrenk 1960]. The

LC_{50} in rats is 350 ppm for 1 hr [NIOSH 1990]. Acutely poisoned animals showed signs of respiratory distress and severe eye irritation before death [NIOSH 1990]. Monkeys and rats exposed for 6 hr/day, 5 days/week to 11 or 25 ppm of cyanogen for 6 months showed no hematologic, clinical, or histopathological changes attributable to exposure [NLM 1992].

2. *Effects on Humans:* Cyanogen causes cellular hypoxia in humans; in lethal amounts, it causes respiratory and central nervous system stimulation, followed by headache, vertigo, agitation followed by combative behavior, coma, convulsions, respiratory arrest, and death [NLM 1992]. Cyanogen reacts readily with cytochrome oxidase in mitochondria which inhibits tissue oxidation resulting in cytotoxic hypoxia. In addition to hypoxia, exposure to cyanogen causes eye, nose, and upper respiratory tract irritation. Exposure to a concentration of 16 ppm for 6 to 8 min caused irritation, but exposure to 8 ppm for the same interval caused no irritation [McNerney and Schrenk 1960].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyanogen may cause pain, redness, and tearing of the eyes, runny nose, and difficult breathing; if the overexposure is severe, the following signs of cyanide poisoning are seen: cherry red lips, tachypnea and hyperpnea (followed by bradycardia), headache, vertigo, agitation, behavioral changes, and convulsions.

2. *Chronic exposure:* The signs and symptoms of chronic overexposure to cyanogen include those of thyroid dysfunction: dizziness, loss of appetite, and weight loss.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL

The following operations may involve cyanogen and may result in worker exposures to this substance:

—Use as an intermediate in organic synthesis

—Use as a fumigant

—Use for welding and cutting heat-resistant metals

—Use as a rocket and missile propellant

The following methods are effective in controlling worker exposures to cyanogen, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyanogen, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and thyroid.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyanogen at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or thyroid.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyanogen exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyanogen on the respiratory system or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Thiocyanate, a metabolite of cyanide, can be measured in the plasma and urine of exposed individuals. However, the levels of thiocyanate in these body fluids that correspond to airborne concentrations of cyanogen have not been determined. Therefore, no biological monitoring test acceptable for routine use has yet been developed for cyanogen.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyanogen is determined

by using a coated XAD-2 tube (150/75-mg sections, 20/60 mesh) coated with 10% (w/w) 2-(hydroxymethyl) piperidine. Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 12 liters is collected. Analysis is conducted by gas chromatography using a nitrogen phosphorus detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cyanogen contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cyanogen should be removed immediately.

A worker who handles cyanogen should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyanogen is handled, processed, or stored.

STORAGE

Cyanogen should be stored in pressurized, secured, airtight containers in a cool, dry, well-ventilated area; the containers must be labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must meet requirements for a Class I flammable liquid. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Ventilation systems used in cyanogen storage areas must be maximally explosion proof. Containers of cyanogen should be protected from physical damage and should be stored separately from water, acids, acid vapors, and oxidizers. Containers should also be protected from shock, direct sunlight, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arresters. Only non sparking tools may be used to handle cyanogen. To prevent static sparks, containers should be grounded and bonded for transfers.

LEAKS

In the event of a leak involving cyanogen, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not get water inside the container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyanogen is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for cyanogen is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of cyanogen per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA [49 CFR 372.30] reporting the amount of cyanogen emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cyanogen is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P031. This substance has been banned from land disposal and may be treated by chemical oxidation, wet air oxidation, or incineration. Cyanogen also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyanogen exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and full-body clothing, as appropriate) should be worn to prevent any skin contact with liquid cyanogen. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyanogen permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyanogen.

Safety glasses, goggles, or face shields should be worn during operations in which cyanogen might contact the eyes. Eyewash fountains and emergency showers should

be available within the immediate work area whenever the potential exists for eye or skin contact with cyanogen. Contact lenses should not be worn if the potential exists for cyanogen exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYANOGEN CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about cyanogen chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  ClCN

- **Structure**

  N≡CCl

- **Synonyms**

  Chlorcyan; chlorine cyanide; chlorocyanide; chlorocyanogen

- **Identifiers**

  1. CAS No.: 506-77-4
  2. RTECS No.: GT2275000
  3. DOT UN: 1589 15 (for cyanogen chloride containing less than 0.9% water)
  4. DOT label: Poison gas; Flammable gas

- **Appearance and odor**

  Cyanogen chloride is a colorless gas with a pungent, penetrating odor. It is shipped in steel cylinders under its own vapor pressure as a liquefied gas. The odor threshold of cyanogen chloride is 1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 61.5
  2. Boiling point (760 mm Hg): 13.8°C (56.8°F)
  3. Specific gravity (water = 1): 1.2 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyanogen chloride): 2.16
  5. Melting point: -6°C (21.2°F)
  6. Vapor pressure at 20°C (68°F): 1,000 to 1,010 mm Hg
  7. Solubility: Soluble in water, alcohol, ether, and all organic solvents

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Moisture, sparks, heat, or flame

2. Incompatibilities: Contact of cyanogen chloride with water, steam, acids, acid salts, or strong oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic substances (such as the oxides of nitrogen cyanide, cyanide, chloride ions, and hydrogen cyanide) may be released in a fire involving cyanogen chloride.

4. Special precautions: Crude cyanogen chloride trimerizes violently to cyanuric chloride if catalyzed by traces of hydrogen chloride or ammonium chloride.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to cyanogen chloride. However, the Hazardous Materials Identification System (HMIS) developed by the National Paint and Coatings Association assigns cyanogen chloride a flammability rating of 4 (severe fire hazard).

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, fog, or standard foam to fight fires involving cyanogen chloride.

Fires involving cyanogen chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of cyanogen chloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Take care not to permit water to contact the cyanogen chloride inside the containers. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyanogen chloride. Chemical protective clothing that is specifically recommended for cyanogen chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing may provide limited protection against fires involving cyanogen chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyanogen chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.3 ppm (0.6 mg/m^3) as a ceiling limit [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyanogen chloride a ceiling limit value of 0.3 ppm (0.75 mg/m^3) [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of severe eye and pulmonary irritation [NIOSH 1992]. The ACGIH limit is based on the risk of irritant, metabolic, and respiratory effects associated with exposure to cyanogen chloride [ACGIH 1993].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyanogen chloride can occur through inhalation, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cyanogen chloride causes eye, mucous membrane, skin, and upper respiratory tract

irritation in animals. Although experimental data on skin absorption are lacking, this substance is reported to cause systemic toxicity when absorbed through the skin in toxic amounts [NLM 1992]. The LC_{50} in rats is 5,400 mg/m^3 (2,700 ppm) for 3 min; in monkeys, it is 4,400 mg/m^3 (2,200 ppm) for 1 min; and in rabbits, it is 6,000 mg/m3 (3,000 ppm) for 7 min [NIOSH 1993]. Animals acutely poisoned with cyanogen chloride show signs of cyanide poisoning and pulmonary edema (dyspnea, bloody nasal exudate, cyanosis) before death [ACGIH 1991].

2. *Effects on Humans:* Cyanogen chloride is a severe eye, skin, mucous membrane, and upper respiratory tract irritant in humans. Exposure to cyanogen chloride also causes cellular hypoxia, as is the case with other cyanides. Exposure to concentrations of cyanogen chloride below 1 ppm (approximately 0.7 ppm) causes burning of the eyes, lacrimation, and severe blepharospasm, local skin irritation, and marked respiratory tract irritation, with hemorrhagic changes and pulmonary edema [Grant 1986; NLM 1992; ACGIH 1991]. Cyanide also interferes with the cell's ability to utilize oxygen, which leads to cellular hypoxia, headache, dizziness, and signs and symptoms that include seizures and coma. Exposure to a cyanogen chloride concentration of 48 ppm for 30 min or to a 159-ppm concentration for 10 min has caused death in humans [Clayton and Clayton 1982]. Repeated inhalation of low (not further specified) concentrations of cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, and weight loss [NLM 1992]. Workers chronically exposed to cyanide salts during metal heat-treating operations developed enlarged thyroid glands [ACGIH 1991; NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyanogen chloride may cause burning of the eyes, tearing, and spasms of the eyelids; a bitter, burning taste followed by a feeling of constriction in the mouth; sweating, salivation, nausea, and vomiting; anxiety confusion, vertigo, giddiness, dizziness, and headache; a bright pink or brick-red coloration to the skin; difficult breathing; increased or decreased blood pressure and heart rate; seizures; and an increase in respiratory rate followed by respiratory arrest.

2. *Chronic exposure:* Chronic overexposure to cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, weight loss, and enlargement of the thyroid.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyanogen chloride and may result in worker exposures to this substance:

—Use in organic synthesis

—Military use as a poison and tear gas

—Use as a warning agent in fumigant gases

—Use in ore refining, in the production of synthetic rubber, and as a metal cleaner

—Use in the Lonza process to produce extremely pure malononitrile

The following methods are effective in controlling worker exposures to cyanogen chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyanogen chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and thyroid. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyanogen chloride at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or thyroid.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyanogen chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyanogen chloride on the respiratory system or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Thiocyanate, a metabolite of cyanide, can be measured in the plasma and urine of exposed individuals. However, the levels of thiocyanate in these body fluids that correspond to airborne concentrations of cyanogen chloride have not been determined. Therefore, no biological monitoring test acceptable for routine use has yet been developed for cyanogen chloride.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyanogen chloride is determined by using a coated XAD-2 tube (150/75-mg sections, 20/60 mesh). The coating is 10% (w/w) 2-(hydroxymethyl)piperidine. Samples are collected at a maximum flow rate of 0.2 liter/min. The sample is then treated with toluene to extract the cyanogen chloride. Analysis is conducted by gas chromatography using a nitrogen phosphorus detector. This method is described in the OSHA Computerized Information System [OSHA 1992].

PERSONAL HYGIENE

Cyanogen chloride can be absorbed through the skin in toxic amounts. Therefore, if cyanogen chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with cyanogen chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyanogen chloride, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles cyanogen chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyanogen chloride or a solution containing cyanogen chloride is handled, processed, or stored.

STORAGE

Cyanogen chloride gas or liquid should be stored in a cool, dry, well-ventilated area in pressurized, airtight containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Cyanogen chloride should not be exposed to direct sunlight. Containers of cyanogen chloride should be protected from shock or physical damage and should be stored separately from water, acids, acid vapors, strong oxidizing agents, heat, sparks, and open flame. Because containers that formerly contained cyanogen chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyanogen chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Evacuate all nonessential personnel.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.
6. Do not get water inside container.
7. For small liquid spills, flush area with flooding amounts of water.
8. For large liquid spills, build dikes far ahead of the spill to contain the cyanogen chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Cyanogen chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for cyanogen chloride is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyanogen chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cyanogen chloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P033. This substance has been banned from land disposal and may be treated by chemical oxidation, wet air oxidation, or incineration. Cyanogen chloride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyanogen chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the

requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and full-body clothing) should be worn as necessary to prevent any skin contact with cyanogen chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyanogen chloride permeation; however, butyl rubber is reported to provide no more than 1 hr of resistance against permeation by cyanogen bromide, a chemically similar substance. Since specific test data are not available for cyanogen chloride, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyanogen chloride.

If cyanogen chloride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyanogen chloride gas or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyanogen chloride. Contact lenses should not be worn if the potential exists for cyanogen chloride exposure.

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OCCUPATIONAL SAFETY AND GUIDELINE FOR CYCLOHEXYLAMINE

INTRODUCTION

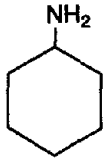
This guideline summarizes pertinent information about cyclohexylamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NH_2$

- **Structure**



- **Synonyms**

Aminocyclohexane, aminohexahydrobenzene, CHA, cyclohexanamine, hexahydroaniline, hexahydrobenzenamine

- **Identifiers**

1. CAS No.: 108-91-8
2. RTECS No.: GX0700000
3. DOT UN: 2357 68
4. DOT label: Flammable liquid; corrosive

- **Appearance and odor**

Cyclohexylamine is a flammable, colorless or yellow liquid with a strong, fishy, amine odor. The odor threshold of cyclohexylamine is 2.6 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 99.17
2. Boiling point (760 mm Hg): 134.5°C (274.1°F)
3. Specific gravity (water = 1): 0.87 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of cyclohexylamine): 3.42
5. Melting point: -17.7°C (0.14°F)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6. Vapor pressure at 20°C (68°F): 11.3 mm Hg

7. Solubility: Completely soluble in water and most organic solvents, including alcohols, ethers, ketones, esters, and chlorinated hydrocarbons; also soluble in peanut oil, mineral oil, acetone, and benzene.

8. Evaporation rate (ether = 1): 82.9

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. Contact of the vapor with air generates an explosive mixture.

2. Incompatibilities: Contact of cyclohexylamine with oxidizers, organic compounds, acid anhydrides, acid chlorides, alkylene oxides, acids, any copper alloy, zinc, or galvanized steel may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving cyclohexylamine.

4. Special precautions: Avoid contact of the vapors with air.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to cyclohexylamine.

1. Flash point: 31°C (88°F) (open cup)

2. Autoignition temperature: 293°C (560°F)

3. Flammable limits in air (% by volume): Lower 1.5; upper 9.4

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to fight fires involving cyclohexylamine. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving cyclohexylamine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cyclohexylamine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclohexylamine. Structural firefighters' protective clothing may provide limited protection against fires involving cyclohexylamine.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclohexylamine [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (40 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclohexylamine a threshold limit value (TLV) of 10 ppm (41 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of severe eye and skin irritation associated with exposure to cyclohexylamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclohexylamine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cyclohexylamine is a severe irritant of the eyes, mucous membranes, and skin in animals. A single drop of a 50% aqueous solution of cyclohexylamine onto the conjunctival sac of a rabbit's eye caused complete destruction of the eye [ACGIH 1991]. When applied to the skin of rabbits, this substance caused severe skin damage [NIOSH 1990]. Although skin sensitization tests in guinea pigs yielded negative results, cyclohexylamine is believed to have weak sensitizing potential [ACGIH 1991; NJDH 1991]. The dermal LD_{50} in rabbits is 277 mg/kg [NIOSH 1990]. Fifty percent of exposed rats died after inhaling a cyclohexylamine concentration of 7,500 mg/m^3 for an unspecified time [NIOSH 1990]. Acutely poisoned animals displayed signs of severe irritation and of central nervous system effects before death [NIOSH 1990]. Rabbits, rats, and guinea pigs exposed for 7 hr/day, 5 days/week to a 1,200-ppm concentration of cyclohexylamine died after a single exposure; however, most animals exposed to a 150-ppm concentration on the same regimen survived for 10 such exposures. Before death, animals of all species exhibited signs of eye and respiratory tract irritation and developed corneal opacities [Clayton and Clayton 1981]. The oral LD_{50} is 156 mg/kg for rats and 224 mg/kg for mice [NIOSH 1990]. In rats, cyclohexylamine has caused reproductive effects in males (reduction in the number and size of litters sired) and females (reduction in pregnancy rate, number of live-born fetuses and post-natal survivors, and birthweight of offspring) [Clayton and Clayton 1981]. In experiments involving rats, mice, and dogs, cyclohexylamine has induced fetotoxic and/or paternal reproductive effects by oral, intraperitoneal, and parenteral administration [NIOSH 1990]. Cyclohexylamine has caused chromosomal breaks in a number of in-vitro test systems [IARC 1980]. Cyclohexylamine has been tested for carcinogenicity in two oral bioassays in mice and four in rats. Based on the results of this research, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of cyclohexylamine in animals is inadequate [IARC 1980].

2. *Effects on Humans:* Cyclohexylamine is a severe irritant of the eyes, skin, mucous membranes, and respiratory tract in humans; it may also cause skin sensitization in some individuals. Cyclohexylamine has caused severe irritation upon contact with the skin; patch tests have shown that this substance is capable of causing skin sensitization [NIOSH 1990; Clayton and Clayton 1981]. Three workers who had been accidentally overexposed to an unspecified concentration of cyclohexylamine experienced symptoms of lightheadedness, drowsiness, anxiety, apprehension, and nausea; one acutely poisoned worker also developed slurred speech and vomited [Hathaway et al. 1991]. Human volunteers who ingested 5 grams of cyclohexylamine a day for 7 or 8 consecutive days showed no adverse effects; workers exposed to airborne concentrations of this substance in the range of 4 to 10 ppm also reported experiencing no symptoms [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyclohexylamine can cause severe irritation of the eyes, with tearing and conjunctivitis; irritation of the respiratory tract, with coughing and difficult breathing; and severe skin irritation, with burns, blisters, redness, swelling, and cell death. Acutely poisoned workers also may experience apprehension, drowsiness, lightheadedness, and vomiting.

2. *Chronic exposure:* Repeated or chronic exposure to cyclohexylamine may cause corneal opacities, dryness and cracking of the skin, and, in some individuals, skin sensitization, with itching, wheals, and redness of the affected areas.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of cyclohexylamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclohexylamine or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclohexylamine and may result in worker exposures to this substance:

—Use as an intermediate in the production of cyclamate sweeteners and textile and rubber chemicals

—Use as a corrosion inhibitor in boiler feed water and oil fields and in the packaging of metal equipment

—Manufacture of dyes, insecticides, plasticizers, emulsifying agents, acid gas absorbents, and dry-cleaning soaps

The following methods are effective in controlling worker exposures to cyclohexylamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveil-

lance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyclohexylamine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society (ATS) [1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclohexylamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclohexylamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclohexylamine on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclohexylamine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyclohexylamine is determined by using a silica gel tube (600/150/150-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 96 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in Method P&CAM 221 of the *NIOSH Manual of Analytical Methods* [NIOSH 1977].

PERSONAL HYGIENE

If cyclohexylamine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with cyclohexylamine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons

laundering the clothes should be informed of the hazardous properties of cyclohexylamine, particularly its potential to cause severe irritation of the eyes and skin.

A worker who handles cyclohexylamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclohexylamine or a solution containing cyclohexylamine is handled, processed, or stored.

STORAGE

Cyclohexylamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of cyclohexylamine should be protected from physical damage and should be stored separately from strong oxidizers (such as chlorine, bromine, and fluorine), acids, copper alloys, lead, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle cyclohexylamine. To prevent static sparks, containers and equipment should be grounded and bonded for transfers. Because containers that formerly contained cyclohexylamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyclohexylamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the cyclohexylamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of cyclohexylamine must comply with EPA's emergency planning requirements [40 CFR Part 355.30].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for cyclohexylamine is 1 or more lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyclohexylamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cyclohexylamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclohexylamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, or gauntlets, as appropriate) should be worn to prevent any skin contact with cyclohexylamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have breakthrough times of less than 1 hr and are not recommended for use with cyclohexylamine: butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl alcohol, polyvinyl chloride, and Viton.

If cyclohexylamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclohexylamine might contact the eyes (e.g., through splashes of solution). Eyewash

fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclohexylamine. Contact lenses should not be worn if the potential exists for cyclohexylamine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLONITE

INTRODUCTION

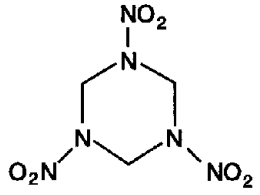
This guideline summarizes pertinent information about cyclonite for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_6N_6O_6$

- **Structure**



- **Synonyms**

RDX; trimethylene trinitramine; cyclotrimethylenenitramine; cyclotrimethylenetrinitramine; hexahydro-1,3,5-trinitro-s-triazine; Hexogen 5W; Hexolite; PBX(AF) 108; sym-trimethylenetrinitramine; trinitrocyclotrimethylene triamine; 1,3,5-trinitro-1,3,5-triazacyclohexane

- **Identifiers**

1. CAS No.: 121-82-4
2. RTECS No.: XY9450000
3. DOT UN: 0072 (wetted with not <25% water, by weight, or desensitized with not <10% phlegmatizer, by weight); 0072 (wetted with not <15 percent water, by weight); 0483 (desensitized)
4. DOT label: Explosive A, corrosive

- **Appearance and odor**

Cyclonite is a white, crystalline powder that is a powerful high explosive. It is also used occasionally as a rodenticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 222.26
2. Boiling point: Data not available
3. Specific gravity (water = 1): 1.82 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 205° to 206°C (401° to 402.8°F)
6. Vapor pressure: 0.0004 mm Hg at 110°C (230°F)
7. Solubility: Insoluble in water, alcohol, benzene, car-

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bon tetrachloride, and carbon disulfide; slightly soluble in ethyl acetate, methanol, ether, and toluene; soluble in acetone

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Shock or heat

2. Incompatibilities: Contact with mercury fulminate detonates cyclonite, and contact with combustibles or strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases (such as the oxides of nitrogen) may be released in a fire involving cyclonite.

4. Special precautions: Cyclonite is one of the most powerful explosives in use today. It must be stored in an explosives magazine and be handled accordingly.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to cyclonite; however, this substance is a dangerous explosion hazard.

1. Flash point: Explodes

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Evacuate the area if cyclonite or materials in the vicinity of cyclonite catch fire. This material is a high explosive and must be handled accordingly. The Fire Department should be called immediately if cyclonite is on fire or materials near this substance catch fire.

Fires involving cyclonite should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclonite.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclonite [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1.5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 3 mg/m^3 as a short-term exposure limit (STEL), both with a "Skin" notation. A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclonite a threshold limit value (TLV) of 1.5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to cyclonite [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of central nervous system effects associated with exposure to cyclonite.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclonite can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cyclonite is toxic to the central nervous system. The oral LD_{50}s in the rat and mouse are 100 mg/kg and 59 mg/kg, respectively; before death, these animals lost weight, became increasingly irritable, and had frequent convulsions. At autopsy, the animals showed lung and gastrointestinal tract congestion [NIOSH 1993; Clayton and Clayton 1981]. Others report an oral LD_{50} of approximately 200 mg/kg in rats [ACGIH 1991]. Seven dogs given 50 mg cyclonite/day, 6 days/week for 6 weeks showed no blood changes and did not develop methemoglobinemia; however, they became excited and irritable, had hyperactive reflexes, and convulsed and collapsed within 1 week of the onset of dosing. At autopsy, no microscopic pathology was seen [Clayton and Clayton 1981; ACGIH 1991]. The low-

est oral dose of cyclonite reported to cause developmental toxicity in the rat is 3 g/kg; 20 mg/kg cyclonite administered on days 6 to 15 of gestation caused fetotoxicity [NIOSH 1993].

2. *Effects on Humans:* In humans, cyclonite is toxic to the central nervous system. Epileptiform seizures have occurred either without warning or after a few days of insomnia, restlessness, and irritability in workers manufacturing cyclonite explosives. The seizures were most frequent in persons inhaling cyclonite-laden dust; the postconvulsive interval was characterized by temporary amnesia, malaise, fatigue, and weakness, but recovery was eventually complete [Clayton and Clayton 1981; ACGIH 1991]. Workers in a large cyclonite manufacturing plant who handled the material in the moist state did not convulse or show other signs of cyclonite poisoning, but they did develop primary irritant and sensitization dermatitis, particularly of the face and eyelids; these skin conditions are believed to have been caused by unidentified intermediates used in the manufacturing process. Patch tests confirmed that cyclonite had not caused the irritation [Clayton and Clayton 1981]. Five workers convulsed or lost consciousness after handling cyclonite in a dusty atmosphere. These workers developed headaches, nausea, vomiting, or unconsciousness either at work or later at home; unconsciousness lasted several minutes to 24 hr and was accompanied by varying degrees of stupor, nausea, vomiting, and weakness. The workers recovered completely, but two of the men became ill again when they were re-exposed to cyclonite [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to cyclonite include headache; irritability; fatigue; weakness; tremors; nausea; dizziness; vomiting; insomnia; unconsciousness; and seizures.

2. *Chronic exposure:* Continued low-level exposure to cyclonite can cause irritability, sleeplessness, and seizures. Cyclonite may cause skin sensitization; if sensitization occurs, very low future exposures can cause itching, the development of a skin rash, and hives.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of cyclonite. Cyclonite can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclonite or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclonite and result in worker exposures to this substance:

—Manufacture, handling, and use of cyclonite explosives, munitions, and solid propellants

—Manufacture, formulation, and application of cyclonite-containing rodenticides

The following methods are effective in controlling worker exposures to cyclonite, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyclonite, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclonite at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies or findings consistent with diseases of the central nervous system or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclonite exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclonite on the central nervous system or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclonite.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyclonite is determined by using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cyclonite contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cyclonite should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyclonite.

A worker who handles cyclonite should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclonite or a solution containing cyclonite is handled, processed, or stored.

STORAGE

Cyclonite should be stored in a permanent explosives magazine. Detached storage is required. Containers of cyclonite should be protected from shock, friction, and physical damage and should be separated from initiator explosives, strong oxidizers, combustibles, shock, heat, sparks, and open flame. Because containers that formerly contained cyclonite may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving cyclonite, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill.
5. Use nonsparking tools for cleanup.
6. Cover the spill with soda ash and spray the area with water. Use a shovel to place the spilled material into a closed container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyclonite is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cyclonite; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyclonite emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although cyclonite is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclonite exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cyclonite. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyclonite permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyclonite.

If cyclonite is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclonite might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclonite. Contact lenses should not be worn if the potential exists for cyclonite exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLOPENTANE

INTRODUCTION

This guideline summarizes pertinent information about cyclopentane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_5H_{10}

- **Synonyms**

  Pentamethylene

- **Identifiers**

  1. CAS No.: 287-92-3
  2. RTECS No.: GY2390000
  3. DOT UN: 1146 27
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Cyclopentane is a flammable, mobile, colorless liquid with a mild, sweet odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 70.13
  2. Boiling point (760 mm Hg): 49.3°C (120.7°F)
  3. Specific gravity (water = 1): 0.75 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyclopentane): 2.42
  5. Melting point: -94°C (-137.2°F)
  6. Vapor pressure at 31°C (87.8°F): 400 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol, ether, acetone, benzene, petroleum ether, carbon tetrachloride.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame

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2. Incompatibilities: Contact of cyclopentane with strong oxidizing agents (such as chlorine, bromine, or fluorine) may cause a reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving cyclopentane.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to cyclopentane.

1. Flash point: -37°C (-35°F) (closed cup)

2. Autoignition temperature: 361°C (682°F)

3. Flammable limits in air (% by volume): Lower, 1.1; upper, 8.7

4. Extinguishant: Use dry chemical, standard foam, or carbon dioxide to fight fires involving cyclopentane. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving cyclopentane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cyclopentane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they heat a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclopentane. Structural firefighters' protective clothing may provide limited protection against fires involving cyclopentane.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclopentane [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 600 ppm (1,720 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for cyclopentane [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclopentane a threshold limit value (TLV) of 600 ppm (1,720 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the risk of CNS depression and skin irritation associated with cyclopentane exposure. The ACGIH limit is based on the risk of narcotic effects associated with exposure to cyclopentane.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclopentane can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Cyclopentane is a central nervous system depressant in animals. Application of cyclopentane to the skin of guinea pigs caused redness and dryness [Clayton and Clayton 1981]. The minimal narcotic concentration in mice is 38.3 ppm; this level of exposure may also cause loss of reflexes and death. The margin of safety between the minimal narcotic dose and the lethal dose is thus very small [Clayton and Clayton 1981]. Exposure to a cyclopentane concentration of 112 to 1,139 ppm for 6 hours/day for 3 weeks caused no effects in male and

female rats; however, exposure to 8,110 ppm for 6 hours/day for 12 weeks caused a decrease in the rate of body weight gain in female rats [Clayton and Clayton 1981].

2. *Effects on Humans:* Cyclopentane is a central nervous system depressant in humans. Because the industrial use of pure cyclopentane is limited and the commercial reagents and solvents that contain cyclopentane also contain other hydrocarbons, there are few toxicologic data on the effects of exposure to the pure substance [ACGIH 1991]. Prolonged contact of this substance with the skin may produce dryness and cracking [NJDH 1989]. Exposure to a 10 to 15 ppm concentration of cyclopentane for an unspecified period is reported to have been tolerated by volunteers [Clayton and Clayton 1981]. The central nervous system effects of exposure to cyclopentane include lightheadedness, dizziness, excitement, incoordination, nausea, vomiting, loss of consciousness, and, if exposure is severe, death due to respiratory failure [Sittig 1985]. One hundred twenty-two Italian shoc factory workers exposed for unspecified periods to unidentified concentrations of glue solvents that contained both cyclopentane and n-hexane developed polyneuropathy; however, the extent to which these polyneuropathies were attributable to cyclopentane exposure is unclear [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to cyclopentane may include lightheadedness, dizziness, excitement, incoordination, nausea, vomiting, stupor, loss of consciousness, and death. Contact with cyclopentane can irritate the skin and eyes.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to cyclopentane include dryness and cracking of the skin. Although cyclopentane has not been adequately evaluated for the possibility of brain and nerve damage following repeated exposures, other solvents and petroleum-based chemicals have been shown to cause such damage, including: reduced memory and concentration, fatigue, sleep disturbances, and reduced coordination.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of cyclopentane. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclopentane or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclopentane and lead to worker exposures to this substance:

—Use in cracking of aromatics

—Use as an intermediate in the production of various chemicals and pharmaceuticals, including analgesics, sedatives, hypnotics, antitumor agents, prostaglandins, depressants, and insecticides

—Use as a component of solvents used for cellulose ethers, motor fuels, and as an azeotropic distillation agent

—Use in the production of cyclopentadiene

—Use as a laboratory chemical

The following methods are effective in controlling worker exposures to cyclopentane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyclopentane, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclopentane at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclopentane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclopentane on the skin and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclopentane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne cyclopentane is made using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 5 liters is collected. The sample is then treated with carbon disulfide to extract the cyclopentane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If cyclopentane contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with cyclopentane should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of cyclopentane.

A worker who handles cyclopentane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclopentane or a solution containing cyclopentane is handled, processed, or stored.

STORAGE

Cyclopentane should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must meet OSHA requirements for Class IB flammable liquids. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of cyclopentane should be protected from physical damage and should be stored separately from strong oxidizing agents (such as chlorine, bromine, and fluorine), heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arresters. Only nonsparking tools may be used to handle cyclopentane. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained cyclopentane may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyclopentane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the cyclopentane for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyclopentane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cyclopentane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of cyclopentane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although cyclopentane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclopentane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowl-

edgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cyclopentane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Butyl rubber and natural rubber have been tested against permeation by cyclopentane and have breakthrough times of less than one hour; therefore, they are not recommended for use with cyclopentane. No other reports were found on the resistance of additional protective clothing materials to cyclopentane permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyclopentane.

If cyclopentane is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclopentane might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclopentane. Contact lenses should not be worn if the potential exists for cyclopentane exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIAZINON

INTRODUCTION

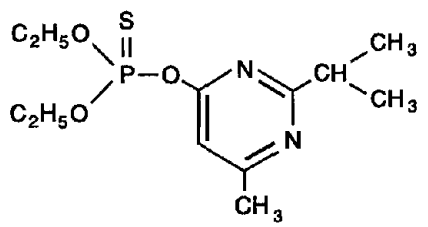
This guideline summarizes pertinent information about diazinon for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{21}N_2O_3PS$

- **Structure**



- **Synonyms**

Diazinone; isopropylmethylpyrimidyl diethyl thiophosphate; Alfa-tox; Basudin; Flytrol; Garden Tox; Knox-out; Nipsan; Oleod-iazinon; O,O-diethyl O-(2-isopropyl-4-methyl-6-pyrimidyl)thionophosphate.

- **Identifiers**

1. CAS No.: 333-41-5
2. RTECS No.: TF3325000
3. DOT NA: 2783 55
4. DOT label: None

- **Appearance and odor**

Pure diazinon is a colorless liquid; however, the technical grade of diazinon has a faint odor and is pale yellow to dark brown in color. Diazinon is an organophosphate pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 304.4
2. Boiling point (0.002 mm Hg): 83° to 84°C (181° to 183°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): 0.00041 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; soluble in organic solvents; miscible with petroleum ether, alcohol, cyclohexane, ether, and benzenes.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Water, heat, sparks, and open flame.

2. Incompatibilities: Contact of diazinon with water, copper-containing compounds, oxidizers, acids, or bases may cause a violent reaction.

3. Hazardous decomposition products: Toxic particulates and gases (such as oxides of nitrogen, phosphorus, sulfur, and carbon monoxide) may be released in a fire involving diazinon.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating to diazinon.

1. Flash point: 180°F (82.2°C)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving diazinon should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of diazinon may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diazinon. Chemical protective clothing specifically recommended for diazinon may not provide thermal protection unless so stated by the manufacturer. Structural firefighters' protective clothing may not provide protection against permeation by diazinon.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diazinon [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has eatablished a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diazinon a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek. The ACGIH also assigns a "Skin" notation to diazinon [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation and cholinesterase inhibition associated with diazinon exposure. The ACGIH limit is based on the risk of cholinesterase inhibition associated with exposure to diazinon.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diazinon can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Diazinon is classified as a moderately toxic organophosphate pesticide [EPA 1989]; it is a cholinesterase inhibitor in experimental animals. Applied to the skin of rabbits under open conditions, 500 mg of diazinon caused moderate systemic toxicity but no primary irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 180 mg/kg

[NIOSH 1993]. The oral LD_{50} in rats is 66 mg/kg, and the LC_{50} in the same species is 3500 mg/m^3 for 4 hours [NIOSH 1993]. In one study, rats fed diazinon at a dose of 50 mg/kg/day for 72 weeks showed complete inhibition of red blood cell cholinesterase activity and marked inhibition of brain cholinesterase activity but no other signs of toxicity [ACGIH 1991]. In another study, rats fed 10, 100, or 1,000 ppm diazinon in the diet for 72 weeks showed no adverse effects [Clayton and Clayton 1981]. Dogs fed diazinon at a dose of 9.3 mg/kg/day promptly lost weight and showed signs of poisoning and developed tremor; at a dose of 4.6 mg/kg/day for 12 weeks, reversible cholinesterase activity was seen in these animals [Hayes 1982]. Rhesus monkeys tolerated diazinon in the diet at a dose of 0.05 mg/kg/day for 2 years without effect; inhibition of both plasma and red blood cell cholinesterase was moderate or erratic when the dose was increased to 0.5 mg/kg/day, and marked decreases in cholinesterase activity occurred at 5 mg/kg/day [Hayes 1982].

2. *Effects on Humans:* Diazinon is an organophosphate pesticide of moderate toxicity [EPA 1989]; it is a cholinesterase inhibitor in humans. In contact with the skin, diazinon may cause allergic skin reactions; this substance has also caused fatalities when absorbed through the skin [NLM 1992]. In a series of tests involving 2 to 4 volunteers, oral diazinon doses of 0.05 mg/kg/day for 28 days caused a 35- to 40-percent reduction in cholinesterase activity in plasma but had no effect on red blood cell cholinesterase activity [ACGIH 1991]. Diazinon administered at an oral dose of 0.02 mg/kg/day for 37 days caused a 14-percent reduction in plasma cholinesterase activity, an amount difficult to distinguish from normal variation [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to diazinon may cause cholinesterase inhibition. The signs and symptoms of cholinesterase inhibition include headache, dizziness, anxiety, restlessness, confusion, bizarre behavior, muscle twitching, weakness, tremor, incoordination, nausea, vomiting, diarrhea, abdominal cramps, sweating, salivation, tearing, blurred vision, constricted pupils, chest tightness, wheezing, cough, rales, bradycardia or tachycardia, and hypertension.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to low doses of cholinesterase inhibitors include, in addition to those listed above, anorexia, weakness, and malaise.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of diazinon. diazinon can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If particulates or vapors, mists, or aerosols of diazinon are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diazinon or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diazinon and may result in worker exposures to this substance:

—Use as a soil insecticide and lawn and garden spray

—Use for insect control on fruits, vegetables, tobacco, forage, field crops, and ornamentals

—Manufacture and formulation of diazinon-containing pesticides

—Use as a pet spray

The following methods are effective in controlling worker exposures to diazinon, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to diazinon, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the cholinesterase activity level of the blood (plasma and red blood cells).

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diazinon at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reductions in plasma or red blood cell cholinesterase activity. To establish a baseline, plasma and red blood cell cholinesterase activity readings should be taken

before the worker is exposed to organophosphate pesticides.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diazinon on plasma or red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of plasma or red blood cell cholinesterase activity is a nonspecific, qualitative indicator of exposure to organophosphorus chemicals such as diazinon. Red blood cell cholinesterase activity can be an indicator either of acute overexposure or of cumulative chronic exposure to diazinon. A red blood cell cholinesterase level that is equal to 70 percent of the worker's preexposure baseline level is recommended by some sources as a biological exposure index for organophosphates.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne diazinon is determined using an OSHA Versatile Sampler (OVS-2), 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh), with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.09 and is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

Diazinon can be absorbed through the skin in toxic amounts. Therefore, if diazinon contacts the skin, workers should repeatedly and vigorously wash the affected areas immediately with soap and water.

Clothing contaminated with diazinon should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles diazinon should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diazinon or a solution containing diazinon is handled, processed, or stored.

STORAGE

Diazinon should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diazinon should be protected from physical damage and should be stored separately from water, oxidizers, acids or bases, heat, sparks, and open flame. Because containers that formerly contained diazinon may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diazinon, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Water spray may be used to reduce vapors.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the diazinon for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

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  Diazinon is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for diazinon is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hour period, in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diazinon emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diazinon is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace

concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diazinon exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with diazinon. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to diazinon permeation. However, permeation tests with similar compounds (other organophosphorus compounds) have shown that a laminate of Viton/neoprene or butyl rubber/neoprene provides good protection against permeation by this group of substances. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to diazinon.

If diazinon is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diazinon might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diazinon.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-n-DIBUTYLAMINOETHANOL

INTRODUCTION

This guideline summarizes pertinent information about 2-n-dibutylaminoethanol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_{10}H_{23}NO$

- **Structure**

  $(C_4H_9)_2NCH_2CH_2OH$

- **Synonyms**

  2-Dibutylaminoethanol; N,N-di-n-butylaminoethanol; beta-n-dibutylaminoethyl alcohol; N,N-dibutylethanolamine; N-N-dibutyl-n-(2-hydroxyethyl)amine; DBAE

- **Identifiers**

  1. CAS No.: 102-81-8
  2. RTECS No.: KK3850000
  3. DOT UN: 2873 55
  4. DOT label: St. Andrew's Cross

- **Appearance and odor**

  2-n-Dibutylaminoethanol is a combustible, colorless liquid with a faint, amine-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 173.3
  2. Boiling point (760 mm Hg): 224° to 232°C (435° to 450°F)
  3. Specific gravity (water = 1): 0.86 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of 2-n-dibutylaminoethanol): 6.0
  5. Melting point: Data not available
  6. Vapor pressure at 20°C (68°F): 0.1 mm Hg
  7. Solubility: Slightly soluble in water; soluble in methanol, ethyl ether, acetone, gasoline, benzene, and ethyl acetate.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of 2-n-dibutylaminoethanol with oxidizing materials causes a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and oxides of nitrogen) may be released in a fire involving 2-n-dibutylaminoethanol.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to 2-n-dibutylaminoethanol.

1. Flash point: 93°C (200°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or foam to fight fires involving 2-n-dibutylaminoethanol.

Fires involving 2-n-dibutylaminoethanol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of 2-n-dibutylaminoethanol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2-n-dibutylaminoethanol. Chemical protective clothing that is specifically recommended for 2-n-dibutylaminoethanol may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving 2-n-dibutylaminoethanol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 2-n-dibutylaminoethanol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (14 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-n-dibutylaminoethanol a threshold limit value (TLV) of 2 ppm (14 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 2-n-dibutylaminoethanol [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on acetylcholinesterase inhibition in vitro and weight loss in animals associated with 2-n-dibutylaminoethanol [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2-n-dibutylaminoethanol can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* 2-n-Dibutylaminoethanol causes irritation of the eyes and skin on acute exposure and liver and kidney damage on longer exposure. In contact with the skin of rabbits, 2-n-dibutylaminoethanol caused severe irritation [NIOSH 1993]. Application of 0.005 ml undiluted 2-n-dibutylaminoethanol to the

eyes of rabbits caused severe corneal injury [Grant 1986]. The oral LD_{50} in rats is 1,070 mg/kg, and the dermal LD_{50} in rabbits is 1,680 mg/kg [NIOSH 1993]. One of 5 rats exposed to a 70-ppm concentration of 2-n-dibutylaminoethanol for 6 hours/day, 5 days/week for 1 week died; in addition, compared with controls, exposed rats had a 57-percent average body weight loss, a 2-fold increase in liver- and kidney-to-body weight ratios, a 10-fold increase in serum bilirubin, a slightly elevated clotting time, and an elevated hematocrit. Exposure to a 22-ppm concentration of 2-n-dibutylaminoethanol on the same regimen for 27 weeks produced no changes in exposed rats [ACGIH 1991]. Rats fed 2-n-dibutylaminoethanol for 5 weeks at doses greater than 0.13 g/kg/day had elevated kidney-to-body weight ratios at autopsy, although no histologic changes were evident [ACGIH 1991].

2. *Effects on Humans:* Exposure to 2-n-dibutylaminoethanol causes irritation of the eyes, nose, throat, and skin in humans [NJDH 1987]. By analogy with the effects caused by chemically similar compounds, exposure to 2-n-dibutylaminoethanol may also cause allergic reactions, such as asthma or skin rashes [NJDH 1987]. In vitro studies show that 2-n-dibutylaminoethanol inhibits the enzyme acetylcholinesterase [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 2-n-dibutylaminoethanol include redness and inflammation of the eyes and eyelids, runny nose, scratchy throat, redness and inflammation of the skin, and acetylcholinesterase inhibition. Symptoms of acetylcholinesterase inhibition include headache, sweating, nausea, vomiting, diarrhea, muscle twitching, coma, and death.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to 2-n-dibutylaminoethanol may include abdominal tenderness, enlarged liver, jaundice, and pus or blood in the urine.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of 2-n-dibutylaminoethanol. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2-n-dibutylaminoethanol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve 2-n-dibutyl-

aminoethanol and lead to worker exposure to this substance:

—Organic synthesis

The following methods are effective in controlling worker exposures to 2-n-dibutylaminoethanol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-n-dibutylaminoethanol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, respiratory system, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-n-dibutylaminoethanol at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with allergies or with diseases of the liver, kidneys, respiratory system, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-n-dibutylaminoethanol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-n-dibutylaminoethanol on the liver, kidneys, respiratory system, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-n-dibutylaminoethanol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 2-n-dibutylaminoethanol is made using a silica gel tube (300/150 mg sections, 45/60 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 24 liters is collected. Immediately after sampling, each section of the tube should be transferred to a separate vial containing 2 milliliters of desorbing solution (0.12 M HCl in 4:1 methanol:water). Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1992] and in Method No. 2007 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If 2-n-dibutylaminoethanol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with 2-n-dibutylaminoethanol should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the irritant properties of 2-n-dibutylaminoethanol.

A worker who handles 2-n-dibutylaminoethanol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2-n-dibutylaminoethanol is handled, processed, or stored.

STORAGE

2-n-Dibutylaminoethanol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of 2-n-dibutylaminoethanol should be protected from physical damage and should be stored separately from oxidizers (such as perchlorates, peroxides, and permanganates), heat, sparks, and open flame. To prevent static sparks, all equipment used in the manufacturing, use, or storage of this substance should be grounded and bonded. Because containers that formerly contained 2-n-dibutylaminoethanol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-n-dibutylaminoethanol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use water spray to reduce vapors.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the 2-n-dibutylaminoethanol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

2-n-Dibutylaminoethanol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of 2-n-dibutylaminoethanol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 2-n-dibutylaminoethanol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although 2-n-dibutylaminoethanol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-n-dibutylaminoethanol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as necessary) should be worn to prevent prolonged or repeated skin contact with 2-n-dibutylaminoethanol. Chemical protective clothing should be selected on the

basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-n-dibutylaminoethanol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-n-dibutylaminoethanol.

If 2-n-dibutylaminoethanol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-n-dibutylaminoethanol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-n-dibutylaminoethanol. Contact lenses should not be worn when working around this material.

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NIOSH [1984]. Method 2007. In: Eller PM, ed. NIOSH manual of analytical methods. 3rd ed., Vol. I. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

NIOSH [1993]. Registry of toxic effects of chemical substances: 2-n-Dibutylaminoethanol. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

OSHA [1992]. Computerized information system. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICHLOROACETYLENE

INTRODUCTION

This guideline summarizes pertinent information about dichloroacetylene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_2Cl_2

- **Structure**

  ClC ≡ CCl

- **Synonyms**

  Dichloroethyne; 1,2-dichloroacetylene

- **Identifiers**

  1. CAS No.: 7572-29-4
  2. RTECS No.: AP1080000
  3. DOT UN: May not be transported.
  4. DOT label: Forbidden

- **Appearance and odor**

  Dichloroacetylene is a combustible, volatile, self-reactive liquid with an isocyanide-like odor. This material is not produced or used commercially; it is an undesirable byproduct of the dehydrochlorination or incomplete incineration of trichloroethylene.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 94.9
  2. Boiling point (760 mm Hg): Explodes on boiling at 32° to 33°C (90° to 91°F)
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: -66° to -64.2°C (-86.8° to -83.6°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; soluble in alcohol, ethanol, and acetone
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: shock, heat, sparks, open flame, acids, oxidizing materials, or contact with the air.

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2. Incompatibilities: Contact of dichloroacetylene with air causes autoxidation and may cause an explosion; contact with acids or oxidizing materials also may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide, phosgene, and chlorine) may be released in a fire involving dichloroacetylene.

4. Special precautions: Dichloroacetylene explodes or ignites on contact with air and explodes if it reaches boiling temperature. Also, in air, unstabilized dichloroacetylene decomposes to phosgene, chloroform, carbon tetrachloride, trichloroacryloyl chloride, and hexachlorobutadiene.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating to dichloroacetylene. However, this substance is known to be spontaneously combustible and to pose a severe explosion hazard when exposed to heat or shock.

1. Flash point: Spontaneously combustible

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use carbon dioxide, water spray, or regular foam. Do not use any chemical extinguishants because dichloroacetylene is shock-sensitive and contact with the surface of dry chemicals may increase its explosive potential. Do not use more water than is necessary to extinguish the fire because it will scatter the fire.

Fires involving dichloroacetylene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dichloroacetylene because poisonous gases (such as phosgene and hydrogen chloride) may be produced in a fire.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dichloroacetylene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.4 mg/m^3) as a ceiling limit. A worker's exposure to dichloroacetylene shall at no time exceed this ceiling level [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dichloroacetylene a ceiling limit value of 0.1 ppm (0.9 mg/m^3), which should not be exceeded during any part of the working day [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer, neurotoxicity, and CNS depression and also the formation of kidney tumors in animals associated with dichloroacetylene exposure. The ACGIH limit is based on the risk of nausea and other systemic effects associated with exposure to dichloroacetylene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dichloroacetylene can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Dichloroacetylene causes kidney and liver damage and cancer in experimental animals. In mice, a 1-hr LC_{50} of 124 ppm and a 4-hr LC_{50} of 19 ppm have been reported. The cause of death was kidney injury [Clayton and Clayton 1981]. A 6-hr LC_{50} in mice of 19 ppm has also been reported [RTECS 1991]. Exposure to dichloroacetylene concentrations of 126, 202, or 307 ppm for 1 hour or to 17 to 23 ppm for 6 hours caused neuropathological changes, kidney and liver damage, and death among rabbits [Clayton and Clayton 1981; IARC 1986]. Rats exposed continuously to a 2.8-ppm concentration of dichloroacetylene for 90 days became emaciated and showed hind limb weakness and kidney injury, and one animal became blind [Grant 1986]. Rats exposed for 6 hours/day, 5 days/week for 6

weeks to a 9.8-ppm concentration of dichloroacetylene (along with 50-ppm trichloroacetylene) or to 15.5 ppm dichloroacetylene (along with 150 ppm trichloroacetylene) were unkempt in appearance and showed signs of respiratory distress; rats in the 15.5-ppm group also showed marked kidney injury at autopsy [Clayton and Clayton 1981]. Dichloroacetylene has been tested for carcinogenicity in inhalation bioassays in mice and rats. Male mice showed dose-related increases in the incidence of adenocarcinomas of the kidney, and rats of both sexes showed an increased incidence of lymphomas and also developed benign tumors of the liver and kidney [IARC 1986]. Based on these data, the International Agency for Research on Cancer has concluded that there is limited evidence that dichloroacetylene is carcinogenic in animals [IARC 1986].

2. *Effects on Humans:* In humans, dichloroacetylene causes eye irritation, headache, nausea, and vomiting as well as nervous system injury and death. As a neurotoxin, dichloroacetylene has an affinity for the cranial nerves [IARC 1986]. Exposure to a 0.5- to 1-ppm concentration of dichloroacetylene for prolonged (not further specified) periods caused nausea in 85 percent of exposed individuals [ACGIH 1991]. Members of a submarine crew developed loss of appetite, nausea that progressed to vomiting, itching around the eyes, headache, sore gums, intense pain in the upper jaw, and facial and oral herpes 3 to 4 days after exposure to dichloroacetylene [IARC 1986]. Tank car cleaners developed fatigue, headache, nausea, and vomiting; these workers also experienced a loss of sensation in the trigeminal nerve distribution that persisted for periods ranging from several days to years [IARC 1986]. Thirteen cases of dichloroacetylene-induced cranial nerve palsy and nine cases of herpes were reported in the 1940s. One patient died 3 days after exposure and a second died 13 days later; autopsy revealed cerebral edema in both of these cases [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dichloroacetylene include redness, inflammation, and itching of the eyes and eyelids, weakness of the eye muscles, headache, nausea, vomiting, sore gums, painful jaws, loss of sensation in the lips and mucous membranes, fatigue, and facial and oral herpes characterized by painful blisters around the mouth.

2. *Chronic exposure:* Based on effects seen in animals, chronic exposure to dichloroacetylene may cause liver or kidney damage, with jaundice, enlarged and tender liver, and pus, protein, or blood in the urine.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dichloroacetylene. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dichloroacetylene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may evolve dichloroacetylene and lead to worker exposures to this substance:

—Thermal dehydrochlorination of trichloroethylene

—Degradation of trichloroethylene, vinylidene chloride, or other hydrocarbons by pyrolysis at temperatures above 70°C (158°F), photolysis, or contact with alkaline materials

—Exposure of trichloroethylene vapors to Hopcalite in a closed environment or to soda lime in closed-circuit anesthesia machines

—Exposure of trichloroethylene liquid to a caustic substance in degreaser tanks

The following methods are effective in controlling worker exposures to dichloroacetylene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to dichloroacetylene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and sensory nerves.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dichloroacetylene at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of

exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the liver, kidneys, or sensory nerves.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dichloroacetylene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dichloroacetylene on the liver, kidneys, or sensory nerves. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dichloroacetylene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne dichloroacetylene is determined using a solid sorbent (charcoal) tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 1 liter is collected. The sample is then treated with carbon disulfide to extract the dichloroacetylene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If dichloroacetylene contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with dichloroacetylene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dichloroacetylene.

A worker who handles dichloroacetylene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dichloroacetylene is handled, processed, or stored.

STORAGE

Dichloroacetylene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must be equipped with explosion-proof electrical equipment and fittings. Containers of dichloroacetylene should be protected from physical damage and should be stored separately from strong acids, oxidizers, potassium, sodium, aluminum powder, heat, sparks, and open flame. Only nonsparking tools may be used to handle dichloroacetylene. An automatic pump should be used to transfer liquid dichloroacetylene from drums or storage containers to process containers. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dichloroacetylene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dichloroacetylene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup

has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Isolate the area of the spill or leak.
3. Remove all sources of heat and ignition.
4. If possible to do so without risk, attempt to stop the leak.
5. Ventilate the area of the spill or leak.
6. For small liquid spills, absorb with earth, sand, vermiculite, or other absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes to contain the spill.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dichloroacetylene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dichloroacetylene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dichloroacetylene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dichloroacetylene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dichloroacetylene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respi-

rator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves, boots, aprons, and gauntlets should be worn as necessary to prevent prolonged or repeated skin contact with dichloroacetylene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dichloroacetylene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dichloroacetylene.

If dichloroacetylene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dichloroacetylene might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dichloroacetylene. Contact lenses should not be worn when the potential for exposure to dichloroacetylene exists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 1,3-DICHLOROPROPENE

INTRODUCTION

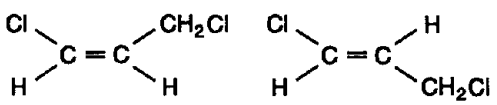
This guideline summarizes pertinent information about 1,3-dichloropropene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_4Cl_2$

- **Structure**



- **Synonyms**

alpha-Chloroallyl chloride; gamma-chloroallyl chloride; 1,3-dichloropropylene; 1,3-dichloropropene-1; Telone; Telone II; Dorlone; alpha,gamma-dichloropropylene.

- **Identifiers**

1. CAS No.: 542-75-6
2. RTECS No.: UC8310000
3. DOT UN: 2047 29
4. DOT label: Flammable liquid

- **Appearance and odor**

1,3-Dichloropropene is a straw-colored liquid with a chloroform-like odor; the commercial product consists of the cis- and trans-isomers in approximately equal parts.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110.98
2. Boiling point (760 mm Hg): 103°C (217°F)
3. Specific gravity (water = 1): 1.2 at 20°C (68°F)
4. Vapor density at 37.8°C (100°F): 3.8
5. Freezing point: -84°C (-119.2°F)
6. Vapor pressure at 25°C (77°F): approximately 28 mm Hg

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7. Solubility: Insoluble in water; soluble in acetone, toluene, octane, carbon tetrachloride, n-heptane, methanol, and benzene.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. The vapors of this substance also form explosive mixtures with air.

2. Incompatibilities: Contact of 1,3-dichloropropene with oxidizers, aluminum or magnesium compounds, or alkaline or corrosive materials causes a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving 1,3-dichloropropene.

4. Special precautions: This substance can polymerize if not stabilized with epichlorohydrin or another stabilizer.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to 1,3-dichloropropene.

1. Flash point: 35°C (95°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 5.3; upper, 14.5

4. Extinguishant: Use water spray, dry chemical, standard foam, or carbon dioxide to fight fires involving 1,3-dichloropropene. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving 1,3-dichloropropene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of 1,3-dichloropropene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container is discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 1,3-dichloropropene. Structural firefighters' protective clothing may provide limited protection against fires involving 1,3-dichloropropene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 1,3-dichloropropene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (5 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure. However, 1,3-dichloropropene has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 1,3-dichloropropene a threshold limit value (TLV) of 1 ppm as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 1,3-dichloropropene [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer associated with 1,3-dichloropropene exposure. The ACGIH limit is based on the risk of kidney injury associated with exposure to 1,3-dichloropropene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 1,3-dichloropropene can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to 1,3-dichloropropene irritates the skin, eyes, and mucous membranes and may cause respiratory tract, liver, and kidney damage in experimental animals. 1,3-Dichloropropene is also carcinogenic in rodents. Exposure to 1,3-dichloropropene vapor (concentration and duration not specified) caused moderate to severe conjunctival irritation and slight to moderate reversible corneal injury in rabbits; applied to the skin of animals of the same species, this substance caused swelling and necrosis [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits for the same solution is 504 mg/kg [ACGIH 1991]. The LC_{50} in rats is 500 ppm for an unspecified period of time, while the 2-hr LC_{50} in mice is 1,033 ppm [NIOSH 1993]. The oral LD_{50} for a 10-percent solution of 1,3-dichloropropene (92-percent purity) in corn oil is 713 mg/kg in male rats and 470 mg/kg in female rats [ACGIH 1991]. Acute inhalation exposure (duration not specified) to concentrations above 2,700 ppm irritated the eyes and nose and caused serious injury to the lungs, liver, and kidneys of rats; exposure to a 1,000 ppm concentration for a period described as "brief" caused severe eye irritation and loss of consciousness, while exposure to 1,000 ppm for 2 hours was lethal to all exposed rats [ACGIH 1991]. Exposure to a 3 ppm concentration of 1,3-dichloropropene for 7-hours a day, 5 days a week for 6 months produced reversible swelling of renal tubular epithelium in rats [ACGIH 1991]. Rats and mice exposed to 0, 93, 32, or 12 ppm for 7 hours a day, 5 days a week for 13 weeks experienced growth depression (high dose rats and female mice) and focal changes of the nasal epithelium in high dose rats (both sexes) and female rats exposed to 32 ppm [Clayton and Clayton 1981]. 1,3-Dichloropropene has been tested in oral carcinogenicity bioassays in both mice and rats. In mice, it produced dose-related increases in the incidences of benign and/or malignant tumors of the urinary bladder, lung, and forestomach. In male rats, it caused dose-related increases in the incidences of benign and malignant forestomach tumors and benign liver tumors; in female rats, it produced benign forestomach tumors [IARC 1986]. Based on this evidence, the International Agency for Research on Cancer has concluded that the evidence for the carcinogenicity of technical-grade 1,3-dichloropropene in animals is sufficient [IARC 1986].

2. *Effects on Humans:* Exposure to 1,3-dichloropropene irritates the eyes, skin, and mucous membranes and may produce respiratory damage in humans. Prolonged skin contact with this substance may cause burns or an itching, red rash [NLM 1992]. After an explosion of a tank car containing this substance, exposed workers immediately experienced coughing and choking, followed by headache, dizziness, irritation of the mucous membranes, and chest discomfort; three of the exposed workers lost consciousness and subsequently died. Pulmonary effects included atelectasis, emphysema, pneumonia, and pulmonary edema [Gosselin et al. 1984]. Individuals exposed to 1,3-dichloropropene during a spill reported headache, fatigue, irritation of the mucous membranes, chest pain, and abdominal discomfort that persisted for up to 2 weeks [Gosselin et al. 1984]. Two firemen previously treated for acute symptoms after exposure to 1,3-dichloropropene subsequently developed malignant histiocytic lymphomas [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 1,3-dichloropropene include pain, redness, and tearing of the eyes; redness and inflammation of the eyelids; redness, burns, and rashes of the skin; headache; fatigue; loss of consciousness; coughing; shortness of breath; chest discomfort; abdominal discomfort; and vomiting. In addition, two cases of malignant histiocytic lymphoma have been reported in workers acutely overexposed to this substance.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to 1,3-dichloropropene include skin burns and cracked, rough, and reddened skin.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of 1,3-dichloropropene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 1,3-dichloropropene or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200)]. All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 1,3-dichloropropene and lead to worker exposures to this substance:

—Use as a soil fumigant

—Use as a chemical intermediate

The following methods are effective in controlling worker exposures to 1,3-dichloropropene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 1,3-dichloropropene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 1,3-dichloropropene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 1,3-dichloropropene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 1,3-dichloropropene on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 1,3-dichloropropene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 1,3-dichloropropene is made using a charcoal solid sorbent tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 5 liters is collected. The sample is then treated with carbon disulfide to extract the 1,3-dichloropropene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in NIOSH Method No. 1003 in the *NIOSH Analytical Methods Manual* [NIOSH 1984], which has been modified for use by OSHA.

PERSONAL HYGIENE

1,3-Dichloropropene can be absorbed through the skin in toxic amounts. Therefore, if 1,3-dichloropropene contacts

the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with 1,3-dichloropropene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of 1,3-dichloropropene, particularly its ability to be absorbed through the skin in toxic amounts.

A worker who handles 1,3-dichloropropene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 1,3-dichloropropene is handled, processed, or stored.

STORAGE

1,3-Dichloropropene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Electrical equipment in storage areas must meet requirements for OSHA Class I flammable liquids. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of 1,3-dichloropropene should be protected from physical damage and should be stored separately from oxidizers, aluminum or magnesium compounds, alkaline or corrosive materials, and heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle 1,3-dichloropropene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained 1,3-dichloropropene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 1,3-dichloropropene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not get water inside the container.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the 1,3-dichloropropene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  1,3-Dichloropropene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for 1,3-dichloropropene is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at

(202) 426-2675 or at (800) 424-8802 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of 1,3-dichloropropene per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 1,3-dichloropropene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. 1,3-Dichloropropene is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.]* and has been assigned EPA Hazardous Waste No. U084. This chemical is approved for land disposal as long as the concentration of 1,3-dichloropropene in the waste or treatment residual does not exceed 18 mg/kg. 1,3-Dichloropropene also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 1,3-dichloropropene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with 1,3-dichloropropene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by 1,3-dichloropropene and may

provide protection for periods greater than 8 hours: polyvinyl alcohol and Viton (fluorocarbon rubber). A material that may withstand permeation for more than 4 but fewer than 8 hours is Teflon (polytetrafluoroethylene). Butyl rubber, natural rubber, neoprene, nitrile rubber, and polyvinyl chloride have demonstrated poor resistance to permeation by 1,3-dichloropropene.

If 1,3-dichloropropene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 1,3-dichloropropene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 1,3-dichloropropene. Contact lenses should not be worn when working with this material.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2,2-DICHLOROPROPIONIC ACID

INTRODUCTION

This guideline summarizes pertinent information about 2,2-dichloropropionic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_3H_4Cl_2O_2$

- **Structure**

  $H_3C—CCl_2—COOH$

- **Synonyms**

  Alatex; Basfapon; BH Dalapon; Basinex; Crisapon; Dalapon; Dalapon 85; Ded-Weed; Devipon; a-dichloropropionic acid; Dowpon; Dowpon M; Gramevin; Kenapon; Liropon; Proprop; Radapon; Revenge; Unipon

- **Identifiers**

  1. CAS No.: 75-99-0
  2. RTECS No.: UF0690000
  3. DOT UN: 1760 60
  4. DOT label: Corrosive

- **Appearance and odor**

  2,2-Dichloropropionic acid is a corrosive, colorless liquid with an acrid odor. The commercial herbicide is a white or tan powder from the sodium and/or magnesium salt. The odor threshold for 2,2-dichloropropionic acid is reported to be 2,500 mg/m^3 (416 ppm).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 142.97
  2. Boiling point (760 mm Hg): 185° to 190°C (365° to 374°F)
  3. Specific gravity (water = 1): 1.4 at 20°C (68°F)
  4. Vapor density: 4.93
  5. Melting point: 174° to 176°C (345.2° to 348.8°F)
  6. Vapor pressure: 10 mm Hg at 40°C (104°F)
  7. Solubility: Very soluble in water, alcohol, and ether.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving 2,2-dichloropropionic acid.

4. Special precautions: 2,2-Dichloropropionic acid is corrosive to iron, aluminum, and copper.

- **Flammability**

The National Fire Protection Association has not issued a fire hazard rating for 2,2-dichloropropionic acid; this substance is not flammable but may burn.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, regular foam, or carbon dioxide to fight fires involving 2,2-dichloropropionic acid. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving 2,2-dichloropropionic acid should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Containers of 2,2-dichloropropionic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2,2-dichloropropionic acid. Structural firefighters' protective clothing may provide limited protection against fires involving 2,2-dichloropropionic acid.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 2,2-dichloropropionic acid [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (6 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for 2,2-dichloropropionic acid [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2,2-dichloropropionic acid a threshold limit value (TLV) of 1 ppm (5.8 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of skin, eye, respiratory, and gastrointestinal irritation associated with 2,2-dichloropropionic acid exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2,2-dichloropropionic acid can occur through inhalation, ingestion, and eye or skin contact; absorption through the skin is said to be "negligible."

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to 2,2-dichloropropionic acid in liquid or vapor form causes corrosion of the eyes and skin; chronic exposure may cause kidney injury. Applied to the skin of rabbits, the sodium salt of 2,2-dichloropropionic acid caused necrosis, and instillation of this substance into the eyes of rabbits caused reversible conjunctival irritation [ACGIH 1991]. The oral LD_{50} in rats is >5,000 mg/kg [NIOSH 1994]. The oral LD_{50} in rats for sodium 2,2-dichloropropionic acid is 9,330 mg/kg (male) and 7,570 mg/kg (female) [Farm Chemicals Handbook 1994]. Exposure to an atmosphere saturated with 2,2-dichloropropionic acid for 7 hours produced no observable effects in rats [ACGIH 1991]. Rats fed 15 mg/kg/day of this substance for 120 days had no ill effects [ACGIH 1991]. Dogs fed 100 mg/kg/day of 2,2-dichloropropionic acid for 1 year and rats given 50 mg/kg/day for the same period showed increased

kidney weights at autopsy [ACGIH 1991]. Dogs given 50 mg/kg/day for 1 year or rats given 15 mg/kg/day for 2 years, showed no significant changes at autopsy [ACGIH 1991].

2. *Effects on Humans:* Exposure to 2,2-dichloropropionic acid causes irritation of the eyes, respiratory tract, and skin, and contact of the eyes or skin with the liquid or vapor can lead to burns. Repeated or prolonged skin contact may cause dermatitis [NJDH 1989]. Exposure to a 2- to 7 ppm concentration of this substance for an unspecified time produced respiratory irritation described as "minimal" [ACGIH 1991], and systemic poisoning caused by acute exposure to an unspecified concentration of this substance resulted in lassitude, vomiting, diarrhea, slowed pulse, and anorexia [NLM 1994].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 2,2-dichloropropionic acid include redness and inflammation of the eyes and eyelids, runny nose, sore throat, coughing, sneezing, difficulty breathing, and reddened and cracked skin. Lassitude, anorexia, vomiting, and diarrhea have also been reported. In contact with the eyes or skin, the vapor or liquid of this substance may cause eye or skin burns.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged skin exposure to 2,2-dichloropropionic acid include reddened, cracked, and blistered skin. Long-term high exposure to 2,2-dichloropropionic acid may affect the liver and kidneys.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Immediately initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of 2,2-dichloropropionic acid! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2,2-dichloropropionic acid or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve 2,2-dichloropropionic acid and lead to worker exposures to this substance:

—Use as a herbicide

The following methods are effective in controlling worker exposures to 2,2-dichloropropionic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2,2-dichloropropionic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, skin, liver, and kidneys. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society (ATS) [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2,2-dichloropropionic acid at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies or findings consistent with diseases of the respiratory system, skin, liver, or kidneys.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2,2-dichloropropionic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2,2-dichloropropionic acid on the

respiratory system, skin, liver, or kidneys. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2,2-dichloropropionic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 2,2-dichloropropionic acid is made using a silica gel tube (150/75 mg sections; 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with deionized water to extract the 2,2-dichloropropionic acid. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1993].

PERSONAL HYGIENE

2,2-Dichloropropionic acid is corrosive; therefore, if this substance contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with 2,2-dichloropropionic acid should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of 2,2-dichloropropionic acid, particularly its potential to cause burns of the skin on contact.

A worker who handles 2,2-dichloropropionic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2,2-dichloropropionic acid or a solution containing 2,2-dichloropropionic acid is handled, processed, or stored.

STORAGE

2,2-Dichloropropionic acid should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of 2,2-dichloropropionic acid should be protected from physical damage and should be stored separately from aluminum and ferric compounds. Because containers that formerly contained 2,2-dichloropropionic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2,2-dichloropropionic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the 2,2-dichloropropionic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

2,2-Dichloropropionic acid is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for 2,2-dichloropropionic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 2,2-dichloropropionic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although 2,2-dichloropropionic acid is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2,2-dichloropropionic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory pro-

tection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with 2,2-dichloropropionic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2,2-dichloropropionic acid permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2,2-dichloropropionic acid.

If 2,2-dichloropropionic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2,2-dichloropropionic acid might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2,2-dichloropropionic acid. Contact lenses should not be worn if the potential exists for 2,2-dichloropropionic acid exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICROTOPHOS

INTRODUCTION

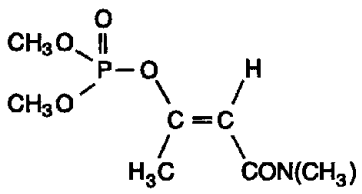
This guideline summarizes pertinent information about dicrotophos for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8H_{16}NO_5P$

- **Structure**



- **Synonyms**

Bidrin; phosphoric acid, dimethyl ester; ester with (E)-3-hydroxy-N,N-dimethylcrotonamide; Bidirl; Carbicron; Ektafos; Oleobidrin; 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl phosphate (E)-isomer; dimethyl 1-dimethylcarbonyl-1-propen-2-yl phosphate

- **Identifiers**

1. CAS No.: 141-66-2
2. RTECS No.: TC3850000
3. DOT NA: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Dicrotophos is a yellow-brown liquid with a mild ester odor. Eighty-five percent of the commercial grade consists of the E-isomer, which is amber in color and more insecticidally active than the Z-isomer.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 237.21
2. Boiling point (760 mm Hg): 400°C (752°F)
3. Specific gravity (water = 1): 1.22 at 15°C (59°F)
4. Vapor density: Data not available
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): 0.0001 mm Hg
7. Solubility: Miscible with water, methylene chloride, ethanol, isopropyl and diacetone alcohols, acetoni-

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

trile, and xylene; slightly soluble in kerosene and diesel fuel.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: None reported.

3. Hazardous decomposition products: Toxic gases (such as oxides of phosphorus and nitrogen) may be released in a fire involving dicrotophos.

4. Special precautions: Dicrotophos is somewhat corrosive to cast iron, mild steel, brass, and stainless steel 304.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating to dicrotophos.

1. Flash point: Greater than 93°C (200°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving dicrotophos.

Fires involving dicrotophos should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of dicrotophos may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicrotophos. Chemical protective clothing that is specifically recommended for dicrotophos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving dicrotophos.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicrotophos [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.25 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for dicrotophos. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicrotophos a threshold limit value (TLV) of 0.25 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to dicrotophos [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to dicrotophos.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dicrotophos can occur through inhalation, ingestion, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Dicrotophos is a highly toxic organophosphorus pesticide that causes cholinesterase inhibition in animals [EPA 1989]. The dermal LD_{50} in rabbits is 168 mg/kg [NIOSH 1993]. The 4-hr LC_{50} in rats is 90 mg/m^3 [NIOSH 1993]. The oral LD_{50} is 13 mg/kg in rats and 11 mg/kg in mice [NIOSH 1993]. Rats fed dicrotophos for 2 years at a dietary level of 1, 10, or 100 ppm showed no effects at the 1-ppm level

but had decreased body weights and reduced cholinesterase activity at the higher levels [ACGIH 1991]. Dogs fed 0.16, 1.6, or 16 ppm for 2 years experienced mild episodes of excessive salivation and, at the highest dose, showed depressed plasma and red blood cell cholinesterase activity [ACGIH 1991].

2. *Effects on Humans:* Dicrotophos is an inhibitor of plasma and red blood cell cholinesterase activity in humans. There are two reports of severe poisoning attributed to dicrotophos, one involving a 41-year-old farmer who had applied this substance to his crops and used it inside his house to control insects, and the other involving a 52-year-old man who ingested a mixture of turpentine and dicrotophos after a drinking bout [Hayes 1982]. Both of these patients eventually recovered after initially responding to treatment and then relapsing seriously [Hayes 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dicrotophos include those of cholinesterase inhibition: headache, nausea, dizziness, anxiety, restlessness, muscle twitching, weakness, tremor, incoordination, vomiting, abdominal cramps, and diarrhea; excessive salivation, sweating, tearing of the eyes, and runny nose also may occur.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to dicrotophos include persistent anorexia, weakness, and malaise, brought on by repeated absorption of dicrotophos in amounts that are not sufficient to cause acute poisoning.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** rinse concentrated solutions, vapors, mists, or aerosols of dicrotophos from the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dicrotophos. Dicrotophos can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If vapors, mists, or aerosols of dicrotophos are inhaled, move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dicrotophos or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dicrotophos and lead to worker exposures to this substance:

—Manufacture, formulation, and application of dicrotophos-containing insecticides and acaricides to cotton, apples, grains, vegetables, ornamentals, shrubs, trees, and other crops

The following methods that are effective in controlling worker exposures to dicrotophos, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to dicrotophos, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood. A pre-exposure red blood cell and plasma cholinesterase activity baseline should also be established.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dicrotophos at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma or red blood cell cholinesterase activity.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dicrotophos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicrotophos on red blood cell and plasma cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophorus compounds such as dicrotophos. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for dicrotophos (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70 percent of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because a patient who has recovered from the acute phase of organophosphorus poisoning remains hypersusceptible to anticholinesterases for as long as several weeks or months, the need for medical monitoring may extend well beyond the acute poisoning episode.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicrotophos is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. The sample is then treated with toluene to extract the dicrotophos. Analysis is conducted by gas chromatography using a flame photometric detector. This method is included in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

Dicrotophos can be absorbed through the skin in toxic amounts. Therefore, if dicrotophos contacts the skin, workers should immediately and repeatedly wash the body (including hair, scalp, and nails) with soap and water. Get medical help immediately.

Clothing contaminated with dicrotophos should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dicrotophos, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles dicrotophos should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dicrotophos or a solution containing dicrotophos is handled, processed, or stored.

STORAGE

Dicrotophos should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must be located at a suitable distance from inhabited buildings, animal shelters, and food stores and must be inaccessible to unauthorized persons. Containers of dicrotophos should be protected from physical damage, heat, sparks, and open flame. Dicrotophos decomposes when stored at temperatures about 25°C to 30°C (77°F to 86°F). Containers should be stacked in a manner that permits free circulation of air at the bottom and insides of the stacks of containers.

SPILLS AND LEAKS

In the event of a spill or leak involving dicrotophos, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use water spray to reduce vapors; do not get water inside the container.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the dicrotophos for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility at which there are 100 lb or more of dicrotophos must comply with EPA's emergency planning requirements [40 CFR 355.40].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for dicrotophos is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the State emergency response commission of any State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicrotophos emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dicrotophos is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require

the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicrotophos exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, full-body covering, and head protection) should be worn as appropriate to prevent any possibility of skin contact with dicrotophos. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dicrotophos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have shown that material made of a laminate of Vitron/neoprene or butyl rubber/neoprene provides good protection against permeation by this group of substances. Since specific test data are not available for dicrotophos, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dicrotophos.

If dicrotophos is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dicrotophos might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dicrotophos.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICYCLOPENTADIENE

INTRODUCTION

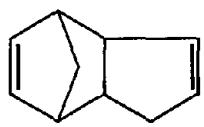
This guideline summarizes pertinent information about dicyclopentadiene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_{10}H_{12}$

- **Structure**



- **Synonyms**

  1,3-Cyclopentadiene, dimer; alpha-dicyclopentadiene (endo form); bicyclopentadiene; biscyclopentadiene; cyclopentadiene dimer; 3a,4,7,7a-tetrahydro-4,7-methanoindene

- **Identifiers**

  1. CAS No.: 77-73-6
  2. RTECS No.: PC1050000
  3. DOT UN: 2048 26
  4. DOT label: Flammable liquid (or solid)

- **Appearance and odor**

  Dicyclopentadiene is a flammable tricyclic compound that exists either as a solid or a clear liquid, depending on temperature. In the solid state, dicyclopentadiene is a colorless, combustible crystalline substance that has a disagreeable camphor-like odor. Dicyclopentadiene exists in two stereoisomeric forms, the endo and exo isomers; the commercial product consists predominantly of the endo isomer. The odor is detectable below 0.2 ppm, but does not become noticeably irritating below 10 ppm.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 132.21
  2. Boiling point (760 mm Hg): 172°C (342°F); depolymerizes at boiling point to form two molecules of cyclopentadiene.

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3. Specific gravity (water = 1): 0.98 at 35°C (95°F)

4. Vapor density (air = 1 at boiling point of dicyclopentadiene): 4.6

5. Melting point: 32°C (89.6°F)

6. Vapor pressure at 20°C (68°F): 1.4 mm Hg

7. Solubility: Insoluble in water; soluble in acetic acid and alcohol; very soluble in ether and carbon tetrachloride.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of dicyclopentadiene with oxidizing agents can cause fires and explosions.

3. Hazardous decomposition products: Thermal-oxidative degradation products can include cyclopentadiene and partial oxidation products of carbon monoxide and carbon dioxide. When heated to decomposition, dicyclopentadiene emits acrid smoke and fumes.

4. Special precautions: Dicyclopentadiene must be inhibited and maintained under an inert atmosphere to prevent hazardous polymerization. In contact with air, especially when heated, dicyclopentadiene forms peroxides; the level of these can be controlled by the addition of an inhibitor.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to dicyclopentadiene.

1. Flash point: 32°C (90°F) (open cup)

2. Autoignition temperature: 503°C (937°F)

3. Flammable limits in air: Lower, 0.8; upper, 6.3

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol-resistant foam, or water fog to fight fires involving dicyclopentadiene.

Fires involving dicyclopentadiene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of dicyclopentadiene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicyclopentadiene. Structural firefighters' protective clothing may provide limited protection against fires involving dicyclopentadiene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicyclopentadiene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (30 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for dicyclopentadiene [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicyclopentadiene a threshold limit value (TLV) of 5 ppm (27 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation associated with dicyclopentadiene exposure. The ACGIH limit is based on the risk of irritation, kidney damage, and pulmonary effects associated with exposure to dicyclopentadiene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dicyclopentadiene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Dicyclopentadiene is an irritant of the eyes and skin and a narcotic on acute exposure; chronic exposure causes kidney and lung damage. Applied to the skin of rabbits, dicyclopentadiene causes moderate to severe irritation; instilled into the rabbit eye, this substance causes mild and reversible irritation [NIOSH 1993; Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 5,080 mg/kg [NIOSH 1993]. The 4-hr LC_{50} is 145 ppm in mice and 372 ppm in rats [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50} is 353 mg/kg in rats and 190 mg/kg in mice [NIOSH 1993]. Acutely poisoned animals showed signs of eye irritation, lost coordination, and convulsed before death [ACGIH 1991]. Rats exposed daily for 10 days to dicyclopentadiene concentrations of 72 or 146 ppm survived, but rats exposed on the same regimen to a concentration of 332 ppm died [ACGIH 1991]. Rats exposed to a 35- or 74-ppm concentration of dicyclopentadiene for 7 hours/day for 89 days showed, at autopsy, kidney damage and some lung involvement [ACGIH 1991]. Leukocytosis was found in rats 96-hr post-subcutaneous administration of dicyclopentadiene [Clayton and Clayton 1981; NLM 1992].

2. *Effects on Humans:* Dicyclopentadiene is an irritant of the eyes, nose, throat, and skin in humans [NJDH 1989]. Exposed workers also experience headaches and other central nervous system effects [NLM 1992]. Workers exposed accidentally to a high but unspecified concentration of dicyclopentadiene experienced headaches for the first two months after exposure but did not continue to experience this symptom indicating a certain degree of inurement [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dicyclopentadiene include redness, tearing, and inflammation of the eyes, sneezing, and coughing. Contact of the skin with this substance causes redness and may cause blistering. Headaches and loss of coordination also may occur after an acute overexposure.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to dicyclopentadiene may include those associated with kidney damage, such as blood, pus, or protein in the urine, or with lung damage, such as difficult breathing, rales, and fluid in the lungs.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dicyclopentadiene. ***Immediately and thoroughly*** flush eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dicyclopentadiene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac

because of possible onset of respiratory depression and seizures.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dicyclopentadiene and lead to worker exposures to this substance:

—Use as a chemical intermediate during chlorinated hydrocarbon pesticide synthesis and to stabilize organophosphorus insecticides

—Use in the production of ferrocene and other metallocene compounds

—Use as an intermediate in the production of plasticizers, elastomers, pharmaceuticals, resins, paints, varnishes, paint driers, and perfumes

—Use as a polyhalogenated flame retardant for plastics

The following methods are effective in controlling worker exposures to dicyclopentadiene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to dicyclopentadiene, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is

exposed to dicyclopentadiene at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, kidneys, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dicyclopentadiene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicyclopentadiene on the eyes, skin, kidneys, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dicyclopentadiene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicyclopentadiene is made using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the dicyclopentadiene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is abstracted in the *OSHA Chemical Information Manual* [OSHA 1987] and can be found in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If dicyclopentadiene contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dicyclopentadiene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dicyclopentadiene, particularly its potential to cause skin irritation.

A worker who handles dicyclopentadiene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dicyclopentadiene or a solution containing dicyclopentadiene is handled, processed, or stored.

STORAGE

Dicyclopentadiene should be stored in a cool, dry, well-ventilated area in tightly sealed, stainless steel containers that are maintained under an inert blanket and are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet requirements for an OSHA Class IB flammable liquid. Only explosion-proof ventilation may be used. Containers of dicyclopentadiene should be protected from physical damage and should be stored separately from oxidizing materials, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dicyclopentadiene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dicyclopentadiene, persons not wearing protective equipment and clothing

should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. Use non-sparking tools for cleanup.
7. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
8. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
9. For large liquid spills, build dikes far ahead of the spill to contain the dicyclopentadiene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) regulatory requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Dicyclopentadiene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dicyclopentadiene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicyclopentadiene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dicyclopentadiene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicyclopentadiene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as

maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with dicyclopentadiene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dicyclopentadiene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dicyclopentadiene.

If dicyclopentadiene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dicyclopentadiene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dicyclopentadiene. Contact lenses should not be worn if the potential exists for dicyclopentadiene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICYCLOPENTADIENYL IRON

INTRODUCTION

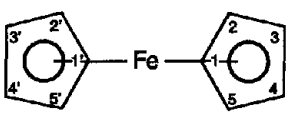
This guideline summarizes pertinent information about dicyclopentadienyl iron for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $(C_5H_5)_2Fe$

- **Structure**



- **Synonyms**

  Ferrotsen; ferrocene; biscyclopentadienyl iron; di-2,4-cyclopentadien-1-yl iron; iron bis(cyclopentadiene); iron bis(cyclopentadienide); iron dicyclopentadienyl; bis(eta(5)-2,4-cyclopentadien-1-yl)-iron

- **Identifiers**

  1. CAS No.: 102-54-5
  2. RTECS No.: LK0700000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Dicyclopentadienyl iron is a flammable, bright orange, crystalline solid with a camphor-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 186.05
  2. Boiling point (760 mm Hg): 249°C (408.2°F) (sublimes above 100°C (212°F))
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: 173°-174°C (343°-345°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; soluble in alcohol, ether, and benzene
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and steam
  2. Incompatibilities: Contact of dicyclopentadienyl iron

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Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

with tetranitromethane may lead to violent explosions. This substance also reacts violently with ammonium perchlorate and mercury (II) nitrate.

3. Hazardous decomposition products: Thermal oxidative decomposition of dicyclopentadienyl iron can produce acrid smoke and irritating fumes.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to dicyclopentadienyl iron. Other sources rate dicyclopentadienyl iron as a moderate fire risk.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: No information is available on the proper extinguishant for fires involving dicyclopentadienyl iron.

Fires involving dicyclopentadienyl iron should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of dicyclopentadienyl iron may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicyclopentadienyl iron.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for dicyclopentadienyl iron is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicyclopentadienyl iron a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and NIOSH limits are based on the risk of mutagenicity associated with exposure to dicyclopentadienyl iron [54 Fed. Reg. 2592; NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dicyclopentadienyl iron can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to dicyclopentadienyl iron may cause liver, red blood cell, and testicular changes in experimental animals. The LC_{50} for an unspecified period of time in rats is greater than 150 mg/m^3 [Hathaway et al. 1991]. The oral LD_{50} is 1,320 mg/kg in rats and 832 mg/kg in mice [NIOSH 1993]. Ten 200 mg/kg oral doses of dicyclopentadienyl iron administered over a 2-week period caused no fatalities in rats [Hathaway et al. 1991]. In a 6-month subchronic study in dogs, oral doses of 30 to 300 mg/kg/day dicyclopentadienyl iron caused hemosiderosis (iron deposits) in the liver [Hathaway et al. 1991; ACGIH 1991]. Dogs exposed to a 300-mg/kg/day dose of dicyclopentadienyl iron for an unspecified period of time developed cirrhosis of the liver; reversible decreases in hemoglobin, packed red cell volume, and red cell count were also seen in these animals within the first 4 weeks of exposure on this regimen [Hathaway et al. 1991]. Testicular hypoplasia developed in dogs given oral dicyclopentadienyl iron doses of 100 mg/kg/day for 6 months [Hathaway et al. 1991; ACGIH 1991]. Dicyclopentadienyl iron is mutagenic in mouse lymphoma test systems [NLM 1992].

2. *Effects on Humans:* No data are available on the

effects of exposure to dicyclopentadienyl iron in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to dicyclopentadienyl iron have been reported in humans.

2. *Chronic exposure:* Based on effects seen in animals, chronic exposure to dicyclopentadienyl iron may cause liver, red blood cell, or testicular damage.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dicyclopentadienyl iron or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dicyclopentadienyl iron and lead to worker exposures to this substance:

—Use as an additive in oil and gasoline fuel to improve efficiency of combustion and eliminate smoke

—Manufacture of rubber, silicone resins, and high-temperature polymers

—Use as coating for missiles and satellites

—Use as a combustion catalyst

The following methods are effective in controlling worker exposures to dicyclopentadienyl iron, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dicyclopentadienyl iron, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood and liver.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dicyclopentadienyl iron at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the blood or liver.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dicyclopentadienyl iron exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicyclopentadienyl iron on the blood or liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dicyclopentadienyl iron.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicyclopentadienyl iron is made using a mixed cellulose ester filter (MCEF) with a 0.8-micron pore size. Samples are collected at a maximum flow rate of 2.0 liters/min until a

maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy (or by inductively coupled argon plasma atomic emission spectroscopy). This method has a sampling and analytical error of 0.16 and is described in OSHA Methods No. ID-121 and No. ID-125G in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If dicyclopentadienyl iron contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with dicyclopentadienyl iron should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dicyclopentadienyl iron.

A worker who handles dicyclopentadienyl iron should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dicyclopentadienyl iron is handled, processed, or stored.

STORAGE

Dicyclopentadienyl iron should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of dicyclopentadienyl iron should be protected from physical damage and should be stored separately from ammonium perchlorate, tetranitromethane, mercury (II) nitrate, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dicyclopentadienyl iron may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dicyclopentadienyl iron, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, take up with activated carbon or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the dicyclopentadienyl iron for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dicyclopentadienyl iron is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dicyclopentadienyl iron; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicyclopentadienyl iron emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dicyclopentadienyl iron is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicyclopentadienyl iron exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as necessary) should be worn to prevent skin contact with dicyclopentadienyl iron. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dicyclopentadienyl iron permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dicyclopentadienyl iron.

If dicyclopentadienyl iron is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dicyclopentadienyl iron might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dicyclopentadienyl iron. Contact lenses should not be worn if the potential exists for dicyclopentadienyl iron exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIETHANOLAMINE

INTRODUCTION

This guideline summarizes pertinent information about diethanolamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_4H_{11}NO_2$

- **Structure**

  $HO(CH_2)_2NH(CH_2)_2OH$

- **Synonyms**

  N,N-Diethanolamine; iminodiethanol; diolamine; diethylolamine; 2,2'-dihydroxydiethylamine; DEA; bis(2-hydroxyethyl)amine; 2,2'iminobisethanol

- **Identifiers**

  1. CAS No.: 111-42-2
  2. RTECS No.: KL2975000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Diethanolamine is a combustible substance that can exist in the form of colorless crystals or a viscous liquid at room temperature. It has a mild, ammonia-like odor and is usually found in liquid form.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 105.14
  2. Boiling point (760 mm Hg): 269°C (516.2°F) (decomposes)
  3. Specific gravity (water = 1): 1.09 at 30°C (86°F)
  4. Vapor density (air = 1 at boiling point of diethanolamine): 3.65
  5. Melting point: 28°C (82.4°F)
  6. Vapor pressure at 20°C (68°F): Less than or equal to 0.01 mm Hg
  7. Solubility: Very soluble in water and alcohol; insoluble in ether and benzene; miscible with acetone and methanol.

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8. Evaporation rate (ether = 1): Greater than 5,000

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. Diethanolamine reacts with carbon dioxide in the air.

2. Incompatibilities: Contact of diethanolamine with oxidizing agents or acidic materials can cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide, carbon dioxide, and oxides of nitrogen) may be released in a fire involving diethanolamine.

4. Special precautions: Diethanolamine is corrosive to copper, copper alloys, zinc, and galvanized iron.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethanolamine.

1. Flash point: 138°C (280°F) (open cup)

2. Autoignition temperature: 661.5°C (1,224°F)

3. Flammable limits in air (% by volume): Lower, 1.6; upper, 9.8

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol foam, or water spray. A solid stream of water or foam directed into burning liquid diethanolamine may cause frothing. Use water spray to cool fire-exposed containers and to dilute liquid to a less flammable solution.

Fires involving diethanolamine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diethanolamine.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diethanolamine [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 3 ppm (15 mg/m^3) as a TWA for up to 10-hr workday and a 40-hr workweek for diethanolamine [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethanolamine a threshold limit value (TLV) of 3 ppm (13 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of eye and skin irritation associated with exposure to diethanolamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diethanolamine can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Diethanolamine is an irritant of the eyes and skin and, when administered orally or intraperitoneally, a kidney and liver toxin in animals. Applied to rabbit skin in a 10-percent solution, diethanolamine caused redness, and the application of more concentrated solutions caused a greater degree of injury [Clayton and Clayton 1981]. Instillation of the undiluted liquid or a 40-percent solution into rabbit eyes caused severe burns; whereas, 15 percent solution produces only minor damage [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 12.2 g/kg [NIOSH 1993]. The oral LD_{50} is 710 mg/kg in rats, 3,300 mg/kg in mice, and 2,200 mg/kg in rabbits [NIOSH 1993]. Animals given large intraperitoneal doses lose the righting reflex, become uncoordinated and cyanotic, and die [Gosselin et al. 1984]. Rats administered 100 or 500 mg/kg

diethanolamine intraperitoneally were autopsied 4 or 24 hours after dosing and showed cytoplasmic vacuolization of the liver and kidneys and, at the higher dose, renal tubular degeneration [Hathaway et al. 1991]. At autopsy, rats fed 0.17 g/kg for 90 days showed cloudy swelling and degeneration of kidney tubules and fatty degeneration of the liver [Hathaway et al. 1991].

2. *Effects on Humans:* Diethanolamine causes irritation of the eyes, nose, and throat in humans, and contact of the skin with this substance can cause minor burns of the skin. Splashed into the eye, diethanolamine may cause severe burns [NJDH 1989].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethanolamine may include redness, inflammation, and tearing of the eyes; inflamed eyelids; coughing; and sneezing. Splashed into the eye, this substance may cause severe eye burns, with corneal necrosis and permanent damage.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged skin contact with diethanolamine include dryness and cracking of the skin and minor burns.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of diethanolamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diethanolamine or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diethanolamine and lead to worker exposures to this substance:

—Use as a liquid detergent in cleaners, polishes, textile specialties, paints, cutting oils, and shampoos

—Use as an absorbent for acid gases

—Use as an emulsifier and dispersing agent in various agricultural chemicals, cosmetics, and pharmaceuticals

—Manufacture of rubber chemicals, surface-active ingredients, and petroleum demulsifiers

—Use as a chemical intermediate in the manufacture of resins and plasticizers

—Use as a humectant and softening agent, in the production of lubricants for the textile industry, and in organic syntheses

The following methods are effective in controlling worker exposures to diethanolamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to diethanolamine, the licensed health care professioanl should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diethanolamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recom-

mended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diethanolamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethanolamine on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diethanolamine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diethanolamine is made using a coated XAD-2 tube (80/40 mg sections, 20/60 mesh); the coating is 10 percent 1-naphthylisothiocyanate (NITC). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with dimethylformamide to extract the diethanolamine derivative. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If diethanolamine contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with diethanolamine should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of diethanolamine, particularly its potential to cause skin irritation.

A worker who handles diethanolamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diethanolamine or a solution containing diethanolamine is handled, processed, or stored.

STORAGE

Diethanolamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diethanolamine should be protected from physical damage and should be stored separately from oxidizers, acidic materials, heat, sparks, and open flame. Because containers that formerly contained diethanolamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethanolamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Mix with inert absorbent materials such as dry sand or vermiculite and place in appropriate containers for disposal.
6. Flush these residues with large quantities of water after neutralizing with sodium bisulfate.

7. Do not flush to sewers or open waterways.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Diethanolamine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR Part 355.40] to notify the National Response Center of an accidental release of diethanolamine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and that manufacture 25,000 lb more or otherwise use 10,000 lb or more of diethanolamine per calendar year are required by EPA [40 CFR Part 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diethanolamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diethanolamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diethanolamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about

the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged skin contact with diethanolamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by diethanolamine and may provide protection for periods greater than 8 hours: butyl rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton®.

If diethanolamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diethanolamine might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diethanolamine. Contact lenses should not be worn if the potential exists for diethanolamine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIETHYLENETRIAMINE

INTRODUCTION

This guideline summarizes pertinent information about diethylenetriamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_4H_{13}N_3$

- **Structure**

  $(NH_2CH_2CH_2)_2NH$

- **Synonyms**

  DETA; N-(2-aminoethyl)1,2-ethanediamine; 2,2'-diaminodiethylamine; aminoethylethandiamine; bis(2-aminoethyl)amine; bis(beta-aminoethyl)amine; N,N-bis(2-aminoethyl)amine; 2,2'-iminobisethylamine

- **Identifiers**

  1. CAS No.: 111-40-0
  2. RTECS No.: IE1225000
  3. DOT UN: 2079 29
  4. DOT label: Corrosive

- **Appearance and odor**

  Diethylenetriamine is a combustible, somewhat viscous, colorless to yellow liquid with an ammonia-like odor. This substance is hygroscopic and strongly alkaline.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 103.17
  2. Boiling point (760 mm Hg): 207°C (405°F)
  3. Specific gravity (water = 1): 0.96 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of diethylenetriamine): 3.56
  5. Melting point: -39°C (-38°F)
  6. Vapor pressure at 20°C (68°F): 0.37 mm Hg
  7. Solubility: Completely soluble in water; soluble in hydrocarbons; insoluble in ether.
  8. Evaporation rate (ether = 1): Greater than 400

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Public Health Service
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National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of diethylenetriamine with oxidizing materials or strong acids may cause a violent reaction; in contact with cellulose nitrate, this substance ignites spontaneously. In contact with silver, cobalt, or chromium compounds, certain diethylenetriamine complexes can be explosive.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon, and hydrocarbons) may be released in a fire involving diethylenetriamine.

4. Special precautions: Diethylenetriamine is corrosive to copper and its alloys.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethylenetriamine.

1. Flash point: 98°C (208°F) (open cup)

2. Autoignition temperature: 358°C (676°F)

3. Flammable limits in air (percent by volume): Lower, 2; upper, 6.7

4. Extinguishant: Use water spray, alcohol foam, carbon dioxide, or dry chemical to fight fires involving diethylenetriamine. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving diethylenetriamine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of diethylenetriamine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if there is discoloration of a container due to fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diethylenetriamine. Structural firefighters' protective clothing may provide limited protection against fires involving diethylenetriamine.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) had not promulgated a permissible exposure limit (PEL) for diethylenetriamine [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for diethylenetriamine of 1 ppm (4 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek with a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethylenetriamine a threshold limit value (TLV) of 1 ppm (4.2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned diethylenetriamine a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of skin and respiratory tract irritation and sensitization associated with exposure to diethylenetriamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diethylenetriamine can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Diethylenetriamine is a severe irritant of the eyes and skin in animals. Application of this substance to rabbit skin caused severe injury, and instillation into the eyes of rabbits caused maximum damage to the cornea [Clayton and Clayton 1981; Grant 1986]. The dermal LD_{50} in rabbits is 1,090 mg/kg [NIOSH 1994]. Acutely poisoned animals convulsed and exhibited signs of gastrointestinal irritation before death [NIOSH 1994]. Rats exposed once to a 300-ppm concentration of diethylenetriamine for 8 hours survived [ACGIH 1986]. The oral LD_{50} in rats is 1,080 mg/kg [NIOSH 1994].

2. *Effects on Humans:* Diethylenetriamine is a severe irritant of the eyes, skin, mucous membranes, and upper respiratory tract and a potent skin and pulmonary sensitizer in humans. In contact with the skin, diethylenetriamine causes severe irritation, with edema and sometimes necrosis [Grant 1986]. A majority of workers chronically exposed to this substance are reported to develop sensitization to it. Exposure to the heated vapor of diethylenetriamine (concentration not specified) causes respiratory tract irritation, and pulmonary sensitization is reported to occur with "relatively high frequency" [NLM 1993; ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethylenetriamine vapors include eye and respiratory tract irritation, with tearing and redness of the eyes, coughing, and difficult breathing. Contact of the eyes or skin with the liquid causes corneal or skin burns, with blistering, swelling, redness, and cell death.

2. *Chronic exposure*: Repeated exposure to diethylenetriamine may cause an asthmatic response in sensitized individuals. Repeated contact of the skin with this substance may cause dermatitis, with redness and scaling, or skin sensitization, accompanied by redness, itching, and the development of wheals.

- **Emergency procedures**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of diethylenetriamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diethylenetriamine or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do *not* permit the victim to drink milk or carbonated beverages!

—Do *not* permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diethylenetriamine and lead to worker exposures to this substance:

—Use as a solvent for sulfur, acid gases, and various resins and dyes

—Use as a saponification agent for acidic materials and as a fuel component

—Use as an intermediate in the manufacture of pharmaceuticals

The following methods are effective in controlling worker exposures to diethylenetriamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to diethylenetriamine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for

the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diethylenetriamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of pulmonary or skin allergies and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diethylenetriamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethylenetriamine on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diethylenetriamine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diethylenetriamine is made using a coated XAD-2 tube (80/40 mg sections, 20/60 mesh); the coating is 10 percent (w/w) 1-naphthylisothiocyanate (NITC). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with dimethylformamide to extract the diethylenetriamine. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Analytical Methods Manual* as OSHA Method No. 60 [OSHA 1985].

PERSONAL HYGIENE

If diethylenetriamine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then by wash with soap and water.

Clothing contaminated with diethylenetriamine should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of diethylenetriamine, particularly its potential to cause burns of the eyes and skin.

A worker who handles diethylenetriamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, applying cosmetics, or using toilet facilities.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diethylenetriamine or a solution containing diethylenetriamine is handled, processed, or stored.

STORAGE

Diethylenetriamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication stan-

dard [29 CFR 1910.1200]. Storage should be in low-fire-risk areas, out of direct sunlight. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of diethylenetriamine should be protected from physical damage and should be stored separately from acids, strong oxidizing agents, heat, sparks, and open flame. Because containers that formerly contained diethylenetriamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethylenetriamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not get water inside the container.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the diethylenetriamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous quantities, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Diethylenetriamine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of diethylenetriamine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diethylenetriamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diethylenetriamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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Good industrial hygiene practice requires that engineer-

ing controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diethylenetriamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with diethylenetriamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by diethylenetriamine and may provide protection for periods greater than 8 hours: butyl rubber, neoprene, and Viton . Natural rubber, nitrile rubber, polyvinyl alcohol, and polyvinyl chloride are not recommended.

If diethylenetriamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diethylenetriamine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diethylenetriamine. Contact lenses should not be worn if the potential exists for diethylenetriamine exposure.

REFERENCES CITED

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIETHYL PHTHALATE

INTRODUCTION

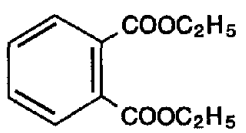
This guideline summarizes pertinent information about diethyl phthalate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_4(COOC_2H_5)_2$

- **Structure**



- **Synonyms**

1,2-Benzenedicarboxylic acid diethyl ester; Anozol; DEP; diethyl o-phthalate; Estol 1550; ethyl phthalate; Neantine; Palatinol A; phthalic acid, diethyl ester; Phthalol; Placidol E; Solvanol; Unimoll DA.

- **Identifiers**

1. CAS No.: 84-66-2
2. RTECS No.: TI1050000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Diethyl phthalate is a flammable, clear, colorless, oily liquid with a bitter, disagreeable taste and a slight ester odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 222.24
2. Boiling point (760 mm Hg): 298°C (568.4°F)
3. Specific gravity (water = 1): 1.12 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of diethyl phthalate): 7.66
5. Melting point: -40.5°C (-40°F)
6. Vapor pressure at 163°C (325°F): 14 mm Hg
7. Solubility: Insoluble in water; miscible with alcohols,

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ketones, esters, and aromatic hydrocarbons; partly miscible with aliphatic solvents.

8. Evaporation rate (ether = 1): Greater than 300

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of diethyl phthalate with strong acids, strong oxidizing agents, nitric acid, permanganates, or water causes a violent reaction.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, carbon dioxide, and various hydrocarbons) may be released in a fire involving diethyl phthalate.

4. Special precautions: Diethyl phthalate attacks some forms of plastic.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethyl phthalate.

1. Flash point: 163°C (325°F) (open cup)

2. Autoignition temperature: 457°C (855°F)

3. Flammable limits in air (percent by volume): Lower, 0.7 (@368°F); upper, data not available

4. Extinguishant: Use dry chemical, water spray, alcohol foam, or carbon dioxide to fight fires involving diethyl phthalate. Water spray and foam are effective but may cause frothing. Water may be used to cool fire-exposed containers.

Fires involving diethyl phthalate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Cool containers from the sides with water until well after the fire is out. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diethyl phthalate.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diethyl phthalate [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethyl phthalate a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on mild toxic effects and smaller than normal fetuses in animals associated with diethyl phthalate exposure; the ACGIH limit is based on the risks of polyneuritis and vestibular dysfunction associated with exposure to diethyl phthalate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diethyl phthalate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to diethyl phthalate causes irritation of the eyes, mucous membranes, and skin and may have reproductive effects in animals. Applied to the skin of rats, 50% of a 30- to 40-mg/kg dose of diethyl phthalate was excreted unchanged within 1 week, and the unexcreted dose remained in the area of application [Hathaway et al. 1991]. Instilled into rabbit eyes, diethyl phthalate caused mild irritation. Guinea pigs exposed to a 511-ppm concentration of diethyl phthalate for 6 hr showed signs of mild skin irritation, and cats exposed to a 10-mg/L concentration of this substance for 5 hr showed signs of nasal irritation [Clayton and Clayton 1981]. The oral LD_{50} is 8,600 mg/kg in rats and 6,172 mg/kg in mice [NIOSH 1993]. Male rats and mice given diethyl phthalate by oral administration developed testicular and other reproductive effects [NIOSH 1993; HSDB 1992]. Diethyl phthalate is mutagenic in bacterial test systems [NIOSH 1993].

2. *Effects on Humans:* Diethyl phthalate has irritant effects on the eyes, mucous membranes, and skin of humans and also causes central nervous system effects in exposed workers. Exposure to the heated vapors of diethyl phthalate is reported to have caused transient nose and throat irritation [ACGIH 1991]. In a study of Russian workers exposed to several phthalates (butyl phthalate, higher alkyl phthalates, dioctyl phthalate, diisooctyl phthalate, and benzyl butyl phthalate) at average ambient concentrations of 1.7 to 66 mg/m^3, 32% of workers were found to have signs and symptoms of polyneuritis; 78% of those workers who reported experiencing adverse effects also showed signs of vestibular dysfunction. The toxic effects seen in these workers were related to the duration of exposure and occurred only after 6 or 7 years of exposure to this group of phthalates [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethyl phthalate include redness and inflammation of eyes and eyelids, runny nose, scratchy throat, headache, dizziness, and nausea.

2. *Chronic exposure:* Chronic exposure to diethyl phthalate may cause signs and symptoms associated with polyneuritis and vestibular dysfunction, including pain, numbness, weakness, and spasms in the arms and legs, dizziness, and nausea.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from concentrated solutions, vapors, mists, or aerosols of diethyl phthalate. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of diethyl phthalate is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diethyl phthalate and lead to worker exposures to this substance:

—Use as a solvent for cellulose acetate in the manufacture of varnishes and dopes

—Use as an alcohol denaturant

—Use as a mosquito repellant, plasticizer in solid rocket propellants, wetting agent, and camphor substitute

—Use as a fixative and solvent in perfumes

The following methods are effective in controlling worker exposures to diethyl phthalate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the period of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to diethyl phthalate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diethyl phthalate at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diethyl phthalate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethyl phthalate on the central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diethyl phthalate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any

changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diethyl phthalate is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) and a glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. The sample is then treated with carbon disulfide to extract the diethyl phthalate. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Chemical Information System [OSHA 1990].

PERSONAL HYGIENE

If diethyl phthalate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, followed by washing with soap and water.

Clothing contaminated with diethyl phthalate should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of diethyl phthalate, particularly its potential to be irritating to the skin and eyes.

A worker who handles diethyl phthalate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diethyl phthalate or a solution containing diethyl phthalate is handled, processed, or stored.

STORAGE

Diethyl phthalate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diethyl phthalate should be protected from physical damage and should be stored separately from acids, bases, strong oxidizing agents, moisture, heat, sparks, and open flame. Because containers that formerly contained diethyl phthalate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethyl phthalate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Ventilate the area of the spill or leak.
3. Take up small spills with paper or other absorbent material for disposal.
4. Build a dike far ahead of the spill area to contain the spill for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Diethyl phthalate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for diethyl phthalate is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hour period, in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of diethyl phthalate per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diethyl phthalate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Diethyl phthalate is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U088. It is approved for land disposal as long as the concentration of diethyl phthalate in the waste or treatment residual does not exceed 28-mg/kg. Diethyl phthalate also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diethyl phthalate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard 29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent

prolonged or repeated skin contact with diethyl phthalate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. 4H (PE/EVAL) has been recommended for use against permeation by diethyl phthalate and may provide protection for more than 4 but fewer than 8 hr. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to diethyl phthalate.

If diethyl phthalate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diethyl phthalate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and washing facilities should be available within the immediate work area whenever the potential exists for eye or skin contact with diethyl phthalate. Contact lenses should not be worn if the potential exists for diethyl phthalate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DINITOLMIDE

INTRODUCTION

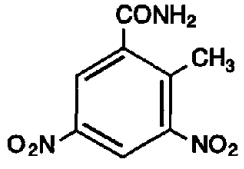
This guideline summarizes pertinent information about dinitolmide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_8H_7N_3O_5$

- **Structure**



- **Synonyms**

  Zoalene; 2-methyl-3,5-dinitrobenzamide; Coccidine A; Coccidot; dinitolmid; Zoamix; 3,5-dinitro-o-toluamide

- **Identifiers**

  1. CAS No.: 148-01-6
  2. RTECS No.: XS4200000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Dinitolmide is a noncombustible, yellowish, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 225.2
  2. Boiling point: Data not available
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: 177°C (350.6°F)
  6. Vapor pressure: Data not available

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7. Solubility: Very slightly soluble in water; soluble in acetone, acetonitrile, dioxane, and dimethylformamide.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving dinitolmide.

4. Special precautions: None reported.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for dinitolmide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving dinitolmide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dinitolmide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dinitolmide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for dinitolmide [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dinitolmide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of liver damage associated with exposure to dinitolmide [NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dinitolmide can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to dinitolmide causes methemoglobinemia and liver changes in animals. The oral LD_{50} in rats is 600 mg/kg [NIOSH 1993]. Rats given a single 150-mg/kg oral dose of dinitolmide developed methemoglobinemia [Gosselin et al. 1984]. Rats fed 6 mg/kg dinitolmide daily for 2 years showed slightly increased liver weights and fatty liver changes in both sexes at autopsy [ACGIH 1991]. Rats fed 3 mg/kg/day showed no adverse effects on growth, mortality rate, tumor incidence, fertility, gestation, or viability [ACGIH 1991]. Beagle dogs fed 10 mg/kg/day for 1 year also showed no effects when evaluated on these measures [ACGIH 1991]. Dinitolmide is mutagenic in bacterial test systems [NIOSH 1993].

2. *Effects on Humans:* In contact with the skin, dinitolmide has caused allergic contact dermatitis in two female poultry attendants [ACGIH 1991]. No other reports on dinitolmide's effects in humans are available.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to dinitolmide have been reported in humans.

2. *Chronic exposure:* Chronic exposure to dinitolmide may cause allergic contact dermatitis. The signs and symptoms include redness, itching, and swelling (hives).

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dinitolmide or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve dinitolmide and lead to worker exposures to this substance:

—Use as a coccidiostat and food additive

The following methods are effective in controlling worker exposures to dinitolmide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dinitolmide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and liver.

  A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dinitolmide at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the skin or liver.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dinitolmide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dinitolmide on the skin or liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dinitolmide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dinitolmide is made using a 37-mm glass fiber filter. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 240 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Laboratory In-House Methods File [ACGIH 1991].

PERSONAL HYGIENE

If dinitolmide contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dinitolmide should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles dinitolmide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dinitolmide or a solution containing dinitolmide is handled, processed, or stored.

STORAGE

Dinitolmide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of dinitolmide should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving dinitolmide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Use a clean shovel and gently place the spilled material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dinitolmide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dinitolmide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dinitolmide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dinitolmide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dinitolmide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing and gloves should be worn to prevent skin contact with dinitolmide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dinitolmide permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dinitolmide.

If dinitolmide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dinitolmide might contact the eyes (e.g., through dust particles). Eyewash fountains should be available within the immediate work area whenever the potential exists for eye contact with dinitolmide.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIPROPYL KETONE

INTRODUCTION

This guideline summarizes pertinent information about dipropyl ketone for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_7H_{14}O$

- **Structure**

  $(CH_3CH_2CH_2)_2CO$

- **Synonyms**

  4-Heptanone; DPK; butyrone; GBL; Heptan-4-one; propyl ketone

- **Identifiers**

  1. CAS No.: 123-19-3
  2. RTECS No.: MJ5600000
  3. DOT UN: 2710 26
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Dipropyl ketone is a combustible, colorless liquid with a pleasant but penetrating odor and a burning taste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 114.2
  2. Boiling point (760 mm Hg): 144°C (291°F)
  3. Specific gravity (water = 1): 0.82 at 15°C (59°F)
  4. Vapor density (air = 1 at boiling point of dipropyl ketone): 3.9
  5. Melting point: -32.6°C (-26.7°F)
  6. Vapor pressure at 20°C (68°F): 5.2 mm Hg
  7. Solubility: Insoluble in water; miscible with alcohol and ether.
  8. Evaporation rate: Data not available.

- **Reactivity**

  1. Conditions contributing to instability: Heat and open flame
  2. Incompatibilities: Contact of dipropyl ketone with oxidizing agents may cause a violent reaction.

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released in a fire involving dipropyl ketone.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to dipropyl ketone.

1. Flash point: 49°C (120°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or alcohol-resistant foam to fight fires involving dipropyl ketone. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving dipropyl ketone should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of dipropyl ketone may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container is discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dipropyl ketone. Structural firefighters' protective clothing may provide limited protection against fires involving dipropyl ketone.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dipropyl ketone [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 50 ppm (235 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for dipropyl ketone [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dipropyl ketone a threshold limit value (TLV) of 50 ppm (233 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on mild toxicity and liver effects in animals caused by exposure to high concentrations of dipropyl ketone [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dipropyl ketone can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Dipropyl ketone is a mild irritant of the eyes and skin and, at high concentrations, a narcotic in animals. Applied to the eyes of rabbits, dipropyl ketone produced mild irritation [NIOSH 1994]. A single application of this substance to the skin of guinea pigs caused slight irritation, but repeated applications of 0.5 ml over a 10-day period caused more serious inflammation [Clayton and Clayton 1982]. In rabbits, the dermal LD_{50} is 5,660 mg/kg [NIOSH 1994]. Fifty percent of rats inhaling a 2,690-ppm concentration of dipropyl ketone for 6 hours (LC_{50}) died; before death, these animals exhibited somnolence and respiratory depression [NIOSH 1994; Clayton and Clayton 1982]. Rats exposed to a dipropyl ketone concentration of 400 ppm for 6 hours showed signs of respiratory depression, and those exposed to 1,600 ppm for the same period became

narcotic [Clayton and Clayton 1982]. The oral LD_{50} in rats is 3,730 mg/kg [NIOSH 1994]. Rats exposed for 6 hours/day, 5 days/week for 2 weeks to a 1,200-ppm dipropyl ketone atmosphere had slightly enlarged livers, although no changes in hematology or serum chemistry were seen [Clayton and Clayton 1982]. Rats gavaged with 2,000 mg/kg dipropyl ketone for 5 days/week for 12 weeks showed signs of severe central nervous system depression and had a reduced rate of weight gain; when the dose was lowered to 1,000 mg/kg, weight gain improved and no clinical abnormalities were seen. At autopsy, however, animals in both dose groups had increased liver and kidney weights and showed hepatocyte hypertrophy [Clayton and Clayton 1982].

2. *Effects on Humans:* Contact of the skin or eyes with the liquid or vapor causes skin or eye irritation [Clayton and Clayton 1982]. Based on effects seen in animals, acute exposure to dipropyl ketone may cause central nervous system depression in humans, and chronic exposure could lead to liver damage [Clayton and Clayton 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dipropyl ketone include redness and inflammation of the eyes and eyelids, coughing and sneezing, and redness and inflammation of the skin. At higher concentrations, dizziness, sleepiness, slowed breathing, and unconsciousness may occur.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to dipropyl ketone may include enlargement of the liver, with jaundice and elevated liver enzymes, and kidney damage, with elevated urinary protein or creatinine levels and blood or pus in the urine. Dryness and cracking of the skin may occur on prolonged or repeated contact.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dipropyl ketone. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dipropyl ketone or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dipropyl ketone and lead to worker exposures to this substance:

—Use as a solvent for nitrocellulose, raw and blown oils, resins, and polymers

—Use in food flavorings and in lacquer formulations

The following methods are effective in controlling worker exposures to dipropyl ketone, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to dipropyl ketone, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, mucous membranes, skin, and central nervous system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dipropyl ketone at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, mucous membranes, skin, or central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dipropyl ketone exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dipropyl ketone on the eyes, mucous membranes, skin, and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dipropyl ketone.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dipropyl ketone is made using a Carbosieve S-III tube (130/65 mg sections; 60/80 mesh). Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 3 liters is collected. The sample is then treated with a carbon disulfide/dimethylformamide mixture (99:1) to extract the dipropyl ketone. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If dipropyl ketone contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dipropyl ketone should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dipropyl ketone, particularly its potential to cause skin irritation.

A worker who handles dipropyl ketone should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dipropyl ketone or a solution containing dipropyl ketone is handled, processed, or stored.

STORAGE

Dipropyl ketone should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of dipropyl ketone should be protected from physical damage and should be stored separately from oxidizing agents, reducing agents, bases, heat, sparks, and open flame. Only nonsparking tools may be used to handle dipropyl ketone. Because containers that formerly contained dipropyl ketone may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dipropyl ketone, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the dipropyl ketone for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Dipropyl ketone is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dipropyl ketone; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dipropyl ketone emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dipropyl ketone is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dipropyl ketone exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with dipropyl ketone. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dipropyl ketone permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dipropyl ketone.

If dipropyl ketone is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dipropyl ketone might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dipropyl ketone. Contact lenses should not be worn if the potential exists for dipropyl ketone exposure.

REFERENCES CITED

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DISULFIRAM

INTRODUCTION

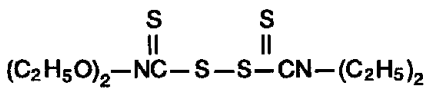
This guideline summarizes pertinent information about disulfiram for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{20}N_2S_4$

- **Structure**



- **Synonyms**

Antabuse; bis(diethylthiocarbamoyl)disulfide; Abstensil; Alcophobin; Antethyl; Aversan; bis((diethylamino)thioxomethyl)disulphide; Disulfan; ethyl thiurad; Thiosan; tetraethylthiram disulfide; tetraethylthiuram disulfide; TTD

- **Identifiers**

1. CAS No.: 97-77-8
2. RTECS No.: JO1225000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Disulfiram is a yellow-white crystalline solid or gray powder that has a slight odor and a slightly bitter taste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 296.54
2. Boiling point (17 mm Hg): 117°C (242.6°F)
3. Specific gravity (water = 1): 1.3 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 70°C (158°F)
6. Vapor pressure: Data not available
7. Solubility: Insoluble in water; soluble in acetone, benzene, chloroform, carbon disulfide, ether, and alcohol; slightly soluble in light petroleum.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: None reported
3. Hazardous decomposition products: Toxic gases (such

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as carbon dioxide, nitrogen dioxide, and sulfur dioxide) may be released in a fire involving disulfiram.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to disulfiram.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving disulfiram should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of disulfiram should be moved from the fire area if it is possible to do so safely. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving disulfiram.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for disulfiram [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned disulfiram a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cytochrome P450 inhibition, d-amino acid inhibition, and aldehyde dehydrogenase inhibition associated with disulfiram exposure [NIOSH 1992]. The ACGIH limit is based on the risk of vasodilation, tachycardia, nausea, and hypotension associated with concomitant exposure to disulfiram and alcohol [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to disulfiram can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to disulfiram produces irritation and central nervous system effects in experimental animals. The oral LD_{50} is 500 mg/kg in rats, 1,980 mg/kg in mice, and 2,050 mg/kg in rabbits [NIOSH 1993]. The major signs of acute toxicity are ataxia, hypothermia, and paralysis [IARC 1976]. A disulfiram solution with a pH of 5.1 caused reversible and slight irritation and corneal opacity when instilled into rabbit eyes [NLM 1993]. In chronic exposure studies, rats fed disulfiram at doses of 1,000 to 2,000 mg/kg/day showed growth retardation, decreased reproductive capacity, and decreased life span [IARC 1976]. In rats exposed to disulfiram at a dose of 100 mg/kg/day from day 3 of gestation, increased fetal resorptions were seen but no teratogenic effects were observed in the surviving offspring [NLM 1993].

2. *Effects on Humans:* The human toxicology of disulfiram may be divided into those effects related to disulfiram alone and those effects associated with the combination of disulfiram and alcohol. Disulfiram alone may produce toxic effects on the nervous system, thyroid, and skin. The combination of disulfiram and alcohol causes a toxic syndrome related to elevated acetaldehyde levels (called the "Antabuse reaction"). The lowest oral dose of disulfiram reported to be lethal in an adult male is 160 mg/kg [NIOSH 1993]. Studies have shown that a small dose of disulfiram can cause a measurable effect on thyroid iodine uptake and also can cause thyroid gland hypertrophy

[Hayes 1982]. Disulfiram can also produce acneform skin rashes, dermatitis, and urticaria [Gilman et al. 1985]. Exposure to disulfiram and concomitant ingestion of alcohol produces a syndrome that begins with a sensation of heat, facial flushing, restlessness, and anxiety and progresses to palpitations, increased heart and respiratory rates, hypotension, chest pain, sweating, nausea, vomiting, weakness, dizziness, and confusion. Atypical and severe reactions have included convulsions, cardiac arrhythmias, myocardial infarction, marked respiratory depression, and acute congestive heart failure [Gosselin et al. 1984]. This syndrome has occurred in workers who have ingested alcohol and then been exposed to disulfiram, as well as to patients exposed to disulfiram as a medication [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to disulfiram may cause headaches, drowsiness, fatigue, dizziness, impaired sexual functioning, a garlic or metallic taste in the mouth, mild gastrointestinal symptoms, depression, psychosis, and confusion. The signs and symptoms of disulfiram-induced peripheral neuropathy may include visual impairment, muscle weakness, numbness, and tingling, and skin reactions to disulfiram exposure may include acneform eruptions, redness, swelling, scaling, and itching.

2. *Chronic exposure:* Chronic exposure to disulfiram may cause identical signs and symptoms to those associated with acute exposure.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if disulfiram or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve disulfiram and lead to worker exposures to this substance:

—Use as a rubber accelerator and vulcanizer

—Use as a medication in the treatment of alcoholism

—Use as a seed disinfectant and fungicide

The following methods are effective in controlling worker exposures to disulfiram, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to disulfiram, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on a history of skin allergies and excessive alcohol intake and on the function and integrity of the central and peripheral nervous systems, eyes, skin, liver, and thyroid.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to disulfiram at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with excessive alcohol intake or with diseases of the eyes, skin, nervous system, liver, or thyroid.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to disulfiram exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of disulfiram on the eyes, skin, nervous system, liver, or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to

a toxic substance or metabolite. Disulfiram and its metabolites can be detected in the blood, urine, and breath of exposed individuals. However, no method of correlating airborne concentrations of disulfiram with concentrations in the blood, urine, or breath has been developed. Therefore, no biological monitoring test acceptable for routine use has yet been developed for disulfiram.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne disulfiram is made using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Samples are extracted with methanol, and analysis is conducted by high-performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If disulfiram contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with disulfiram should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles disulfiram should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where disulfiram or a solution containing disulfiram is handled, processed, or stored.

STORAGE

Disulfiram should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of disulfiram should be protected from physical damage and should be stored separately from phenols, flammable substances, heat, sparks, and open flame. Because containers that formerly contained disulfiram may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving disulfiram, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate the area of the spill or leak.
4. Collect powdered material in the most convenient manner and deposit in sealed containers.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Disulfiram is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of disulfiram; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of disulfiram emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although disulfiram is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of disulfiram exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with disulfiram. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to disulfiram permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to disulfiram.

If disulfiram is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which disulfiram might contact the

eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with disulfiram. Contact lenses should not be worn if the potential exists for disulfiram exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIURON

INTRODUCTION

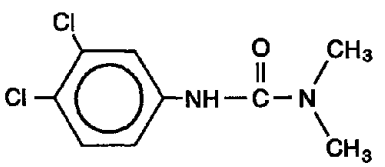
This guideline summarizes pertinent information about diuron for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{10}Cl_2N_2O$

- **Structure**



- **Synonyms**

3-(3,4-Dichlorophenyl)-1,1-dimethylurea; dichlorfenidim; Crisuron; Diurex; Karmex Diuron Herbicide; Telvar Diuron Weed Killer

- **Identifiers**

1. CAS No.: 330-54-1
2. RTECS No.: YS8925000
3. DOT UN: 2767 55
4. DOT label: None

- **Appearance and odor**

Diuron is a white, odorless, crystalline solid. It is available commercially as an 80 percent wettable powder or a 35 percent aqueous suspension.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 233.1
2. Boiling point (760 mm Hg): 189° to 190°C (372.2° to 374°F) (decomposes)
3. Specific gravity: Data not available
4. Vapor density: Data not available
5. Melting point: 158° to 159°C (316.4° to 318.2°F)
6. Vapor pressure at 50°C (122°F): 0.0000031 mm Hg

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7. Solubility: Slightly soluble in water and hydrocarbons; soluble in acetone.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving diuron.

4. Special precautions: Diuron hydrolyzes in fairly strong acids.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for diuron; this substance is not flammable.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, CO_2, water spray, fog, or standard foam to fight fires involving diuron.

Fires involving diuron should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of diuron should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diuron. Chemical protective clothing that is specifically recommended for diuron may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving diuron.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diuron [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for diuron [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diuron a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation associated with diuron exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diuron can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Acute exposure to diuron causes mild skin irritation and narcosis in animals, and chronic exposure to this substance may cause blood changes and spleen and liver enlargement. In contact with the unbroken skin of guinea pigs, diuron caused no irritation; in contact with broken skin, however, this substance caused a moderate degree of irritation [EPA 1987]. The dermal LD_{50} in rabbits is greater than 2,500 mg/kg [EPA 1987]. Instilled into the eyes of rabbits, diuron caused no irritation [EPA 1987]. The oral LD_{50} in rats is 1,017 mg/kg [NIOSH 1993]. Acutely poisoned animals showed signs of central

nervous system depression before death [EPA 1987]. Rats fed daily doses of diuron ranging from 2,000 to 8,000 ppm in the diet for 42 days showed decreased red blood cell counts and hemoglobin values (2,000 ppm or greater), growth retardation (4,000 ppm or greater), and increased mortality (8,000 ppm) [EPA 1987]. Rats fed diuron at a dietary dose of 5,000 ppm for 90 days showed reduced body weights, enlarged spleens, splenic hemosiderosis, and chronic methemoglobinemia [EPA 1987]. Rats fed diuron at a dietary dose of 250 ppm or higher for 2 years showed growth retardation, decreased red blood cell counts, decreased hemoglobin values, splenic hemosiderosis, and increased mortality [EPA 1987]. Oral exposure to 250 mg/kg/day of an 80 percent diuron solution on days 6 through 15 of gestation caused a statistically significant increase in wavy rib abnormalities in the offspring of rats [EPA 1987].

2. *Effects on Humans:* No information on the toxic effects of occupational exposure to diuron is available. Based on effects seen in animals, acute exposure to diuron would be expected to cause mild skin irritation and headaches, drowsiness, and incoordination in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to diuron have been reported in humans.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to diuron have been reported in humans.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diuron or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diuron and lead to worker exposures to this substance:

—Manufacture, formulation, and use as a pre-emergence herbicide

—Use as a general weed killer and as a soil sterilant

—Use as a sugar cane flowering suppressant

The following methods are effective in controlling worker exposures to diuron, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to diuron, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diuron at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with adverse effects on the blood.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diuron exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diuron on the blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to

a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diuron.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diuron is made using an OSHA Versatile Sampler (OVS-2) 13 mm XAD-2 tube (270/140 mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If diuron contacts the skin, workers should wash the affected areas immediately with soap and water.

Clothing contaminated with diuron should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles diuron should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diuron or a solution containing diuron is handled, processed, or stored.

STORAGE

Diuron should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diuron should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained diuron may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diuron, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Water spray may be used to reduce vapors.
6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the diuron for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Diuron is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for diuron is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employees are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diuron emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diuron is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diuron exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional informa-

tion about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, and coveralls, as appropriate) should be worn to prevent skin contact with diuron. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to diuron permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to diuron.

If diuron is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diuron might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diuron. Contact lenses should not be worn if the potential exists for diuron exposure.

REFERENCES CITED

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ENDOSULFAN

INTRODUCTION

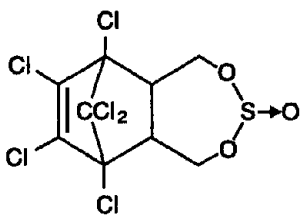
This guideline summarizes pertinent information about endosulfan for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_6Cl_6O_3S$

- **Structure**



- **Synonyms**

6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide; Benzoepin; Beosit; Chlorthiepin; Crisulfan; Cyclodan; Devisulphan; Endocel; Endosol; Ensure; Hildan; Insectophene; Kop-Thiodan; Malix; Niagara 5,462; Thiodan; Thifor; Thiosulfan; Tiovel

- **Identifiers**

1. CAS No.: 115-29-7
2. RTECS No.: RB9275000
3. DOT NA: 2761 55
4. DOT label: Poison

- **Appearance and odor**

Endosulfan is a tan, semi-waxy solid that is a mixture of two isomers; it may have a slight, sulfur dioxide-like odor. This substance is an organochlorine pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 406.95
2. Boiling point: 106°C (222.8°F) at 0.7 mm Hg
3. Specific gravity (water = 1): 1.75 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 108° to 110°C (226.4° to 230°F) alpha isomer; 208° to 210°C (406.4° to 410°F) beta isomer; 70° to 100°C (158° to 212°F) mixture
6. Vapor pressure at 25°C (77°F): 0.00001 mm Hg
7. Solubility: Insoluble in water; moderately soluble in most organic solvents; soluble in xylene, kerosene, chloroform, acetone, and alcohol.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, open flame, moisture, and air.

2. Incompatibilities: Edosulfan is incompatible with acids and alkalies (which can cause it to hydrolyze) and is corrosive to iron.

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of sulfur) may be released in a fire involving endosulfan.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association had not assigned a fire hazard rating for endosulfan; this substance may burn, but it does not ignite readily.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, standard foam, or fog to fight fires involving endosulfan. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving endosulfan should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of endosulfan may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving endosulfan. Chemical protective clothing that is specifically recommended for endosulfan may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving endosulfan.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for endosulfan [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for endosulfan. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned endosulfan a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to endosulfan [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of convulsions associated with endosulfan exposure and the high toxicity in experimental female animals caused by endulsofan exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to endosulfan can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Endosulfan causes central nervous system, kidney, liver, and testicular effects in animals. The dermal LD_{50} in rabbits is 90 mg/kg [NIOSH 1993]. The 4-hr LC_{50} is 80 mg/m^3 in rats [NIOSH 1993]. The oral LD_{50} is 18 mg/kg in rats and 7.4 mg/kg in mice [NIOSH 1993]. Farm animals ingesting endosulfan (dose not specified) exhibited ataxia and seizures [Hayes 1982]. Some rats given

oral doses (10 mg/kg/day) died after 15 days; at 5 mg/kg/day, rats survived but showed signs of liver damage at autopsy [Hayes 1982]. In one oral feeding study, rats tolerated endosulfan doses of 2.5 mg/kg/day for 24 months without effects, but feeding at a dose of 5 mg/kg/day for the same period reduced the growth and survival rates in female rats, caused changes in the kidneys of male rats, and caused blood changes in rats of both sexes [ACGIH 1991]. Oral doses of 10 mg/kg/day for 15 days caused degeneration of the somniferous tubules and a significant decrease in testis weight among male rats [ACGIH 1991]. A dose of 5 mg/kg/day or higher on gestation days 6 through 14 increased the mortality of rat dams and increased the rates of resorption and skeletal abnormalities in their offspring [ACGIH 1991].

2. *Effects on Humans:* Endosulfan causes central nervous system and respiratory effects in humans. The estimated lethal dose of endosulfan in humans is 50 to 500 mg/kg [Gosselin et al. 1984]. Suicides and accidental deaths have been described after acute exposure to endosulfan; these episodes resulted in gagging, vomiting, diarrhea, agitation, convulsions, foaming at the mouth, difficulty breathing, apnea, cyanosis, and loss of consciousness [Hayes 1982]. One or more seizures occurred in nine workers exposed to endosulfan while performing various tasks, including the bagging of a 50 percent water-wettable endosulfan powder. These workers experienced a prodromal syndrome consisting of malaise, nausea, vomiting, dizziness, weakness, confusion, and headache. Recovery occurred within a few days [ACGIH 1991; Hayes 1982]. In a case involving subchronic exposure, a worker cleaning vats that contained endosulfan residues developed malaise, fainting spells, and seizures; after 4 months of exposure, this worker had three consecutive seizures that resolved after emergency medical treatment. Later, gross cognitive deficits and agitation were diagnosed; 2 years later, this worker continued to have memory impairment, nominal aphasia, and poor visual-motor coordination [Aleksandrowicz 1979].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute oral exposure to endosulfan include malaise, nausea, vomiting, dizziness, weakness, confusion, headache, nervousness, agitation, tremor, seizures, convulsions, diarrhea, difficult breathing, cyanosis, and loss of consciousness. Inhalation exposure may cause nausea, confusion, excitement, flushing, and dry mouth.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to endosulfan include malaise, fainting, seizures, convulsions, agitation, cognitive impairments, and respiratory impairment (including shortness of breath and cough).

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Endosulfan can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if endosulfan or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve endosulfan and lead to worker exposures to this substance:

—Use as an insecticide for deciduous fruits, nuts, cotton and vegetables, ornamentals, tea, and coffee

—Use as an acaricide against aphids, thrips, beetles, foliar feeding larvae, cutworms, leafhoppers, the tsetse fly, and slugs

The following methods are effective in controlling worker exposures to endosulfan, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to endosulfan, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to endosulfan at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as

well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to endosulfan exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of endosulfan on the central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for endosulfan.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne endosulfan is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) and an enclosed glass fiber filter. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 60 liters is collected. Analysis is conducted by gas chromatography using an electron capture detector. This method is described in the OSHA Computerized Information System [OSHA 1993].

PERSONAL HYGIENE

Endosulfan can be absorbed through the skin in toxic amounts. Therefore, if endosulfan contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with endosulfan should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of endosulfan, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles endosulfan should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where endosulfan or a solution containing endosulfan is handled, processed, or stored.

STORAGE

Endosulfan should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of endosulfan should be protected from physical damage and should be stored separately from alkalies, acids, heat, sparks, and open flame. Because containers that formerly contained endosulfan may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving endosulfan, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into of the spill to contain the endosulfan for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

The owners and operators of a facility must comply with EPA's emergency planning requirements if 1 lb or more of endosulfan is present at the facility.

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for endosulfan is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of any State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of endosulfan emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Endosulfan is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. P050. Endosulfan is approved for land disposal as long as the concentration of endosulfan in the waste or treatment residual does not exceed 0.13 mg/kg. Endosulfan also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, rele-

vant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of endosulfan exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with endosulfan. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. One source recommends the use of protective gloves and clothing made of Viton or neoprene for protection against permeation by endosulfan.

If endosulfan is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which endosulfan might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with endosulfan. Contact lenses should not be worn if the potential exists for endosulfan exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHION

INTRODUCTION

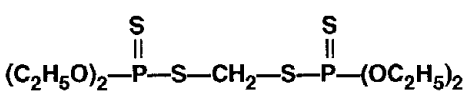
This guideline summarizes pertinent information about ethion for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{22}O_4P_2S_4$

- **Structure**



- **Synonyms**

bis(S-(Diethoxyphosphinothioyl)mercapto)methane; ethyl methylene phosphorodithioate; O,O,O',O'-tetraethyl S,S'-methylene di(phosphorodithioate); phosphorodithioic acid, O,O-diethyl ester, S,S-diester with methanedithiol; Bladan; Diethion; Embathion; Ethanox; Ethodan; Fosfono 50; Hylemox; Niagra 1240; Nialate; Rhodiacide; Rhodocide; Soprathion

- **Identifiers**

1. CAS No.: 563-12-2
2. RTECS No.: TE4550000
3. DOT NA: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Ethion is a colorless liquid that is odorless when pure. Ethion is marketed in several forms: as granules, a wettable powder, a dust, and in various oil solutions and combinations with other materials. Technical grade ethion has a very disagreeable odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 384.48
2. Boiling point (760 mm Hg): Decomposes above 150°C (302°F)
3. Specific gravity (water = 1): 1.22 at 20°C (68°F)
4. Vapor density: Data not available
5. Freezing/melting point: -12° to -13°C (8.6° to 10.4°F)

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6. Vapor pressure at 25°C (77°F): 0.0000015 mm Hg

7. Solubility: Slightly soluble in water; soluble in acetone, methyl alcohol, ethyl alcohol, xylene, chloroform, methylated naphthalene, and petroleum oils.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Ethion is incompatible with alkaline formulations.

3. Hazardous decomposition products: Toxic gases (such as oxides of sulfur and phosphorus) may be released in a fire involving ethion.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for ethion.

1. Flash point: 176°C (348.8°F)

2. Autoignition temperature: Data not available

3. Flammable limits: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, fog, or standard foam to fight fires involving ethion. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving ethion should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of ethion may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving ethion. Chemical protective clothing that is specifically recommended for ethion may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving ethion.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethion [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.4 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for ethion. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ethion a threshold limit value (TLV) of 0.4 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to ethion [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cholinesterase inhibition and toxic effects on the nervous, respiratory, and digestive systems associated with ethion exposure [NIOSH 1992]. The ACGIH limit is based on the risk of organophosphate poisoning associated with exposure to ethion [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ethion can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Ethion is an organophosphate pesticide that produces its effects by inhibiting cholinesterase activity in the central nervous system.

Instilled into the eyes of rabbits, 0.05 ml of ethion caused immediate irritation without corneal injury [NLM 1993]. The dermal LD_{50} is 62 mg/kg in rats and 915 mg/kg in guinea pigs [NIOSH 1993]. The LC_{50} in rats is 864 mg/m3 for an unspecified period [NIOSH 1993]. The oral LD_{50} is 13 mg/kg in rats and 40 mg/kg in mice [NIOSH 1993]. Rats fed ethion at a dietary level of 300 ppm for 28 days developed marked cholinesterase inhibition, and those fed dietary levels of 600 to 1,500 ppm showed complete cholinesterase inhibition [NLM 1993].

2. *Effects on Humans:* Ethion is an organophosphate pesticide that causes cholinesterase inhibition in humans. The lethal oral dose in humans is estimated to be 50 to 500 mg/kg [Gosselin et al. 1984]. Ethion is reported to have caused organophosphate poisoning in peach and grape pickers who were applying this pesticide [ACGIH 1991]. In an in vitro culture, ethion caused a significant increase in the frequency of sister chromatid exchanges in human lymphoid cells [NLM 1993].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute oral exposure causes severe gastrointestinal effects, such as cramps, diarrhea, nausea, and anorexia. Acute inhalation causes wheezing, difficult breathing, blurred vision, constricted pupils, and tearing. Acute dermal exposure causes localized twitching and sweating. Severe overexposure by any route can cause respiratory paralysis, coma, and death.

2. *Chronic exposure:* Repeated exposure to small amounts of ethion may cause acetylcholine buildup and lead to the signs and symptoms of poisoning described above for acute exposure.

- **Emergency procedures:**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately*** rinse concentrated solutions, vapors, mists, or aerosols of ethion from the eyes with large amounts of water for at least 15 min, occasionally lifting the lower and upper eyelids. If irritation persists, get medical attention as soon as possible.

2. *Skin exposure:* Ethion can be absorbed through the skin in lethal amounts. ***Immediately*** remove all contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion esposure:* Take the following steps if ethion or a solution containing this substance is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ethion and lead to worker exposures to this substance:

—Use as an insecticide and acaricide for citrus fruit, apples, nuts, deciduous fruit, and cotton

—Use as a cattle dip for ticks and as a treatment for buffalo flies

—Use for the control of aphids, mites, scales, thrips, leafhoppers, maggots, and foliar feeding larvae on a wide variety of food, fiber, and ornamental crops

The following methods are effective in controlling worker exposures to ethion, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ethion, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on red blood cell and plasma cholinesterase activity.

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ethion at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reductions in red blood cell or plasma cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ethion exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethion on red blood cell or plasma cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific qualitative indicator of exposure to organophosphorus chemicals such as ethion. Inhibition of RBC ChE can be an indicator either of acute overexposure or of cumulative chronic exposure, depending on the intensity and duration of exposure. Individual pre-exposure levels of enzyme activities should be determined by measuring RBC ChE activity in blood samples collected on two occasions (at least 3 days apart) before exposure begins or following at least 30 days without exposure; the same method and laboratory should be used for sampling and analysis. An RBC ChE activity level that is equal to 70 percent of the individual's baseline is recommended by some sources as a Biological Exposure Index (BEI) for exposure to organophosphorus chemicals.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne ethion is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 480 liters is collected. The sample is then treated with toluene to extract the ethion. Analysis is conducted by gas chromatography using a flame photometric detector. This method is described in the OSHA Computerized Information System [OSHA 1993] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

Ethion can be absorbed through the skin in toxic amounts. Therefore, if ethion contacts the skin, workers should wash the affected areas repeatedly and vigorously with soap and water.

Clothing contaminated with ethion should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of ethion, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles ethion should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where ethion or a solution containing ethion is handled, processed, or stored.

STORAGE

Ethion should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of ethion should be protected from physical damage and should be stored separately from food or feed products, heat, sparks, and open flame. Because containers that formerly contained ethion may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethion, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the ethion for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous waste, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

The owners or operators of a facility must comply with EPA's emergency planning requirements [40 CFR 355.30] if 1,000 lb or more of ethion are present.

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for ethion is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of ethion emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although ethion is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ethion

exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only those respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with ethion. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon has been tested for use against permeation by ethion and may provide protection for periods greater than 4 but less than 8 hours. Natural rubber has a breakthrough time of less than 1 hr and is therefor not recommended for use against permeation by ethion.

If ethion is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ethion might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ethion.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENE GLYCOL

INTRODUCTION

This guideline summarizes pertinent information about ethylene glycol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_2H_6O_2$

- **Structure**

  CH_2OHCH_2OH

- **Synonyms**

  1,2-Dihydroxyethane; 1,2-ethanediol; 2-hydroxyethanol; ethane-1,2-diol; ethylene alcohol; ethylene dihydrate; glycol; monoethylene glycol; glycol alcohol; Lutrol-9; Macrogol 400BPC; Norkool; Dowtherm SR 1

- **Identifiers**

  1. CAS No.: 107-21-1
  2. RTECS No.: KW2975000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Ethylene glycol is a combustible, slightly viscous, colorless liquid with a sweet taste and no odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 62.1
  2. Boiling point (760 mm Hg): 197.6°C (387.7°F)
  3. Specific gravity (water = 1): 1.11 at 20°C (68°F)
  4. Vapor density: 2.1
  5. Melting/freezing point: -13°C (8.6°F)
  6. Vapor pressure at 20°C (68°F): 0.06 mm Hg
  7. Solubility: Miscible in water, ethanol, glycerol, acetic acid, and acetone; slightly soluble in ether; practically insoluble in benzene and its homologs, chlorinated hydrocarbons, petroleum ether, and oils.
  8. Evaporation rate: Data not available

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. Ethylene glycol that is heated or misted into the air presents a moderate fire and explosion hazard.

2. Incompatibilities: Ethylene glycol can react dangerously with chlorosulfonic acid, oleum, sulfuric acid, and strong oxidizing agents such as perchlorates, peroxides, permanganates, chlorates, and nitrates.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving ethylene glycol.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to ethylene glycol.

1. Flash point: 115°C (240°F) (open cup); 111°C (232°F) (closed cup)

2. Autoignition temperature: 398°C (748°F)

3. Flammable limits in air (percent by volume): Lower, 3.2; upper, data not available

4. Extinguishant: Use water spray, dry chemical, "alcohol" foam, or carbon dioxide to fight fires involving ethylene glycol. Water or foam may cause frothing. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to dilute spills to noncombustible mixtures.

Fires involving ethylene glycol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of ethylene glycol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container is discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving ethylene glycol. Structural firefighters' protective clothing may provide limited protection against fires involving ethylene glycol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethylene glycol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for ethylene glycol [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) assigns ethylene glycol a ceiling limit value of 50 ppm (127 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of respiratory tract irritation associated with exposure to ethylene glycol [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ethylene glycol can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to airborne concentrations of ethylene glycol causes eye and upper respi-

ratory tract irritation, and ingestion causes central nervous system depression, kidney and liver injury, and fetotoxic and developmental effects in experimental animals. In contact with the eyes or skin of rabbits, ethylene glycol caused irritation classified as mild [NIOSH 1994]. The dermal LD_{50} in rabbits is 9,530 mg/kg [NIOSH 1994]. The oral LD_{50} is 4,700 mg/kg in rats, 5,500 mg/kg in mice, and 6,610 mg/kg in guinea pigs [NIOSH 1994]. Dogs and cats given oral doses of ethylene glycol developed ataxia, vomiting, polydipsia, and seizures before losing consciousness [NLM 1993]. Exposure to a 12-mg/m^3 concentration of ethylene glycol continuously for 90 days, however, caused a moderate to severe degree of eye irritation in rabbits and rats [ACGIH 1991]. Dietary levels of ethylene glycol as high as 2 percent for 2 years caused decreased life span, calcium oxalate bladder stones, and kidney and liver damage in rats; the no-effect level in this study was no more than 0.2 percent in the diet (100 mg/kg/day) for 2 years [Clayton and Clayton 1981]. Several studies in rats and mice given oral doses of ethylene glycol during pregnancy have shown fetotoxic and developmental effects [NIOSH 1994].

2. *Effects on Humans:* Exposure to ethylene glycol vapor or mist causes eye, nose, and upper respiratory tract irritation in humans. In one report, reversible conjunctival inflammation occurred after ethylene glycol was splashed into a worker's eye [Hathaway et al. 1991]. By ingestion or percutaneous absorption, ethylene glycol causes central nervous system effects, liver and kidney damage, and cardiopulmonary effects. Loss of consciousness and nystagmus were reported among 9 of 38 women exposed to ethylene glycol vapor, and 5 of these workers also showed lymphocytosis [Clayton and Clayton 1981]. Throat irritation, headache, and backache were reported in human volunteers exposed to a mean concentration of ethylene glycol mist ranging from 1.4 to 27 ppm for 20 to 22 hours/day for 4 weeks. At a concentration of 60 ppm, symptoms were common; at 80 ppm, coughing and a sensation of tracheal burning became intolerable [ACGIH 1991]. Ingestion of a large amount (100 ml or more) of ethylene glycol produces three well-documented stages of toxicity. In Stage 1, which occurs within 30 minutes, nausea and vomiting, slurred speech, ataxia, nystagmus, lethargy, and a faint, sweetish odor on the breath develop. Coma, convulsions, and respiratory depression or cardiovascular collapse also may occur at this stage. In Stage 2, cardiopulmonary effects progress and cyanosis, pulmonary edema, and congestive heart failure may develop. In Stage 3, acute tubular necrosis develops, with oxaluria or anuria; these signs may progress to uremia and renal failure [Clayton and Clayton 1981; Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute airborne exposure to ethylene glycol include redness and irritation of the eyes and eyelids, sore throat, runny nose, cough, headache, and backache. Massive ingestion causes nausea; vomiting; slurred speech; ataxia; nystagmus; lethargy; impaired vision; a faint, sweet odor on the breath; coma; convulsions; elevated body temperature; elevated heart and respiratory rates; hypotension; agitation; confusion; cyanosis; tremor; areflexia; muscle twitches or contractions; crystalluria; hematuria; proteinuria; oxaluria; anuria; uremia; and cardiopulmonary collapse.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to ethylene glycol have been reported in humans.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of ethylene glycol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform car-

diopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if ethylene glycol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by touching the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ethylene glycol and lead to worker exposures to this substance:

—Use as antifreeze in cooling and heating systems

—Use as a vehicle for pharmaceutical preparations, food extracts, and flavoring essences and as a component of skin lotions, a substitute for glycerin, and an ingredient in various powders

—Use in electrolytic condensers as a solvent for boric acid and borates

—Use as a solvent in the paint and plastics industries

—Use in the formulation of printers' inks, stamp pad inks, and inks for ball point pens

—Use in the synthesis of safety explosives, glyoxal, unsaturated ester-type alkylated resins, plasticizers, elastomers, synthetic fibers (terylene and dacron), and synthetic waxes

—Use as an industrial humectant

The following methods are effective in controlling worker exposures to ethylene glycol, depending on the feasibility of implementation:

— Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls,

and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ethylene glycol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, upper respiratory tract, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ethylene glycol at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, upper respiratory tract, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ethylene glycol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethylene glycol on the eyes, upper respiratory tract, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although several of the metabolites of ethylene glycol can be detected in body fluids (serum, urine, blood) of exposed individuals, levels of these metabolites do not correlate well with airborne concentrations of ethylene glycol. Therefore, no biological monitoring test acceptable for routine use has yet been developed for ethylene glycol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne ethylene glycol is made using a glass fiber filter in a Swinnex (TM) cassette, followed by a silica gel tube (520/260 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a minimum collection time of 5 minutes is reached. As soon as possible after sampling, the filter is removed from the cassette and placed in a vial with a Teflon-lined cap containing 1 mL of 2% isopropanol in water. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1993] and in Method No. 5500 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If ethylene glycol contacts the skin, workers should flush the affected areas with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with ethylene glycol should be

removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of ethylene glycol, particularly its potential to be irritating to the eyes, nose, and upper respiratory tract.

A worker who handles ethylene glycol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where ethylene glycol or a solution containing ethylene glycol is handled, processed, or stored.

STORAGE

Ethylene glycol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Since some containers can affect the color of this material, resin-coated steel, glass, aluminum, or stainless steel containers should be used for storage. Containers of ethylene glycol should be protected from physical damage and should be stored separately from chlorosulfonic or sulfuric acid, oxidizing agents such as perchlorates, peroxides, permanganates, chlorates, nitrates, moisture, heat, sparks, and open flame. Because containers that formerly contained ethylene glycol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethylene glycol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the ethylene glycol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Ethylene glycol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of ethylene glycol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of ethylene glycol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of ethylene glycol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-

261.24. Although ethylene glycol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ethylene glycol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with ethylene glycol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against ethylene glycol and have demonstrated good-to-excellent resistance for periods of greater than 8 hr: natural rubber, butyl rubber, neoprene, polyvinyl chloride, nitrile rubber, polyethylene, Teflon, Viton, Saranex, and Barricade. 4H and Responder have demonstrated good-to-excellent resistance for periods of greater than 4 hr and less than 8 hr. Polyvinyl alcohol has a breakthrough time of 1 to 4 hr and should be used with caution against ethylene glycol.

If ethylene glycol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ethylene glycol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ethylene glycol. Contact lenses should not be worn if the potential exists for ethylene glycol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLIDENE NORBORNENE

INTRODUCTION

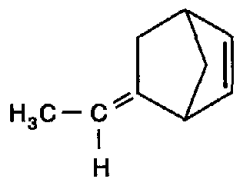
This guideline summarizes pertinent information about ethylidene norbornene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_9H_{12}

- **Structure**



- **Synonyms**

  5-Ethylidene-2-norbornene; 5-ethylidenebicyclo(2,2,1)hept-2-ene; ENB

- **Identifiers**

  1. CAS No.: 16219-75-3
  2. RTECS No.: RB9450000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Ethylidene norbornene is a combustible, colorless to white liquid with a turpentine-like odor. An odor threshold for ethylidene norbornene has been reported in the range of 0.007 to 0.014 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 120.2
  2. Boiling point (760 mm Hg): 147.6°C (298°F)
  3. Specific gravity (water = 1): 0.896 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of ethylidene norbornene): 4.1
  5. Freezing/Melting point: -80°C (-112°F)
  6. Vapor pressure at 20°C (68°F): 4.2 mm Hg
  7. Solubility: Data not available
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and oxygen.

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2. Incompatibilities: Contact of ethylidene norbornene with oxygen can cause violent reactions.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide) may be released in a fire involving ethylidene norbornene.

4. Special precautions: Because of its reactivity, ethylidene norbornene must be stabilized with tert-butyl catechol.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for ethylidene norbornene; however, other sources report that this substance is combustible.

1. Flash point: 38.33°C (101°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving ethylidene norbornene. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving ethylidene norbornene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving ethylidene norbornene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethylidene norbornene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (25 mg/m^3) as a ceiling limit for ethylidene norbornene. The ceiling limit should not be exceeded during any part of the workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ethylidene norbornene a ceiling limit value of 5 ppm (25 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation associated with ethylidene norbornene exposure and renal, urogenital, and bone marrow effects found in animals exposed to ethylidene norbornene [NIOSH 1992]. The ACGIH limit is based on the risk of eye and nose irritation associated with exposure to ethylidene norbornene [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ethylidene norbornene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Ethylidene norbornene causes irritation of the eyes and skin, as well as liver and testicular toxicity in animals. In contact with the skin of rabbits, ethylidene norbornene caused a mild degree of skin irritation [NIOSH 1994]. The dermal LD_{50} in rabbits is 8,189 mg/kg [NIOSH 1994]. In contact with the eyes of rabbits, this substance produced transient conjunctival irritation [Grant 1986]. The 4-hr LC_{50} is 1,246 ppm in rats and 732 ppm in mice [NIOSH 1994]. The oral LD_{50} is 2,527 mg/kg in rats and 3,250 mg/kg in mice. Dogs exposed to a 93-ppm concentration of ethylidene norbornene for 7 hours/day, 5 days/week, for a total of 89 exposures showed slight blood changes and, at autopsy, hepatic lesions and testicular atrophy [Hathaway et al. 1991]. When dogs were exposed to a concentration of 61 ppm on the same regimen, less severe lesions of these organs were seen at post mortem. At an ethylidene norbornene concentration of 22 ppm, no damage was noted [Hathaway et al. 1991]. Twenty-one of twenty-four rats inhaling a 237-ppm concentration of ethylidene norbornene on the same schedule died. Liver

lesions, atrophy of the testicles, and hydrothorax were observed. No deaths occurred from 90 ppm, but liver lesions were evident [ACGIH 1991].

2. *Effects on Humans:* Ethylidene norbornene causes eye, nose, and upper respiratory tract irritation in humans. Volunteers exposed for 30 minutes to a 6-ppm concentration of ethylidene norbornene reported transient eye irritation, and, at a concentration of 11 ppm, both eye and nose irritation were experienced [ACGIH 1991]. In contact with the skin, ethylidene norbornene caused reddening and defatting [USCG 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to ethylidene norbornene include redness and inflammation of the eyes and eyelids, runny nose, scratchy throat, and redness and inflammation of the skin.

2. *Chronic exposure:* Repeated exposure to ethylidene norbornene may damage the liver, kidneys, and lungs in humans.

- **Emergency procedures:**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposures to concentrated solutions, vapors, mists, or aerosols of ethylidene norbornene. ***Immediately and thoroughly*** flush eyes with large amounts of water occasionally lifting the lower and upper eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if ethylidene norbornene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ethylidene norbornene and may lead to worker exposures to this substance:

—Manufacture of pharmaceuticals and pesticides

—Preparation of specialty resins

—Use as the third monomer in ethylene-propylene diene monomer elastomers

The following methods are effective in controlling worker exposures to ethylidene norbornene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ethylidene norbornene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, upper respiratory tract, reproductive system, skin, liver, and kidneys. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ethylidene norbornene at or below the prescribed exposure limit. A licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, respiratory tract, skin, liver, or kidneys or disturbances in reproductive function.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ethylidene norbornene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethylidene norbornene on the eyes, respiratory tract, skin, liver, kidneys, or reproductive function. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ethylidene norbornene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history

interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

No sampling and analytical method is available to determine a worker's exposure to airborne ethylidene norbornene.

PERSONAL HYGIENE

If ethylidene norbornene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with ethylidene norbornene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of ethylidene norbornene, particularly its potential to be irritating to the skin.

A worker who handles ethylidene norbornene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where ethylidene norbornene or a solution containing ethylidene norbornene is handled, processed, or stored.

STORAGE

Ethylidene norbornene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Ethylidene norbornene must be stored under an inert (oxygen free) atmosphere (i.e., a nitrogen atmosphere) or be stabilized with tert-butyl catechol. Containers of ethylidene norbornene should be protected from physical damage and should be stored away from oxygen, heat, sparks, and open flame. Because containers that formerly contained ethylidene norbornene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethylidene norbornene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors.
6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the ethylidene norbornene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Ethylidene norbornene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental

Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of ethylidene norbornene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of ethylidene norbornene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although ethylidene norbornene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ethylidene norbornene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with ethylidene norbornene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to ethylidene norbornene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to ethylidene norbornene.

Safety glasses, goggles, or face shields should be worn during operations in which ethylidene norbornene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ethylidene norbornene. Contact lenses should not be worn if the potential exists for ethylidene norbornene exposure.

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