

OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
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NOTE TO THE READER

These 35 occupational safety and health guidelines are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes data on chemical names and synonyms, chemical and physical properties, exposure limits, signs and symptoms of exposure, as well as recommendations for medical monitoring, respiratory and personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers achieve a sound occupational health program.

The recommendations and information contained in these guidelines may be superseded as new information becomes available; readers are advised to regard these recommendations as general guidelines and should not rely on them for achieving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

This document supplements the 1981 publication entitled 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). Readers may wish to insert each guideline at the appropriate place in that 3-volume set.

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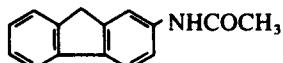
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-ACETYLAMINOFLUORENE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 2-acetylaminofluorene for workers, employers, and 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 Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₁₅H₁₃NO

• **Structure:** 

• **Synonyms:** 2-AAF; 2-acetamidofluorene; 2-acetylaminofluorene; N-acetyl-2-aminofluorene; 2-(acetylamino)fluorene; N-FAA; 2-FAA

• **Identifiers:** CAS 53-96-3; RTECS AB9450000; DOT not assigned

• **Appearance:** Tan, crystalline solid

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 223.29
2. Melting point: 194°C (381.2°F)
3. Insoluble in water

• **Flammability**

Extinguishant: Dry chemical, carbon dioxide

• **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 2-acetylaminofluorene; however, the OSHA standard requires implementation of stringent controls wherever 2-acetylaminofluorene or solid or liquid mixtures containing at least 0.1% by weight or volume of 2-acetylaminofluorene are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1014, 2-Acetylaminofluorene. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have an assigned threshold limit value (TLV®) for 2-acetylaminofluorene.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

2-Acetylaminofluorene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

1. *Effects on animals:* Subchronic or chronic oral administration of 2-acetylaminofluorene in dogs, rats, or hamsters produced cancers of the bladder or liver. In rats, cancers of the kidneys, pancreas, pelvis, salivary glands, eyes, ear ducts, and auditory and sebaceous glands were also found. In all animals that developed cancer from exposure to 2-acetylaminofluorene, the potent carcinogenic metabolite N-hydroxy-2-acetylaminofluorene was produced. Single oral doses of 2-acetylaminofluorene to pregnant rats on days 8-12 of gestation induced fetal malformations (hydrocephaly).
2. *Effects on humans:* Five cancer patients treated with single oral doses of 2-acetylaminofluorene produced the N-hydroxy-2-acetylaminofluorene metabolite, indicating that 2-acetylaminofluorene may be metabolized in humans as it was in animals that developed cancer from exposure to 2-acetylaminofluorene.

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RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to 2-acetylaminofluorene, the 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 skin, liver, urinary tract, and reproductive system.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-acetylaminofluorene. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional exami-

nations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-acetylaminofluorene. Because the metabolite N-hydroxy-2-acetylaminofluorene has been identified in both animals and humans administered 2-acetylaminofluorene, consideration should be given to monitoring for this metabolite in workers who may be exposed to 2-acetylaminofluorene.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to 2-acetylaminofluorene may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• Method

There is no NIOSH-validated sampling or analytical method for 2-acetylaminofluorene.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory type hoods" or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting

the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system. If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 2-acetylaminofluorene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 2-acetylaminofluorene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-acetylaminofluorene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 2-acetylaminofluorene from materials and equipment. Contaminated materials should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1014:

Areas where 2-acetylaminofluorene is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 2-acetylaminofluorene, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only

authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 2-acetylaminofluorene which are not in an isolated system, laboratory type hood, or other system affording equivalent protection against the entry of 2-acetylaminofluorene into regulated areas, non-regulated areas, or the external environment are prohibited.

In operations involving "laboratory type hoods" or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 2-acetylaminofluorene shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to non-regulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 2-acetylaminofluorene from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-acetylaminofluorene may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 2-acetylaminofluorene

Operation	Controls
During use in research and laboratory facilities	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 2-acetylaminofluorene, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to 2-acetylaminofluorene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-acetylaminofluorene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to 2-acetylaminofluorene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use. If 2-acetylaminofluorene gets on the skin, wash it immediately with soap and water. If 2-acetylaminofluorene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 2-acetylaminofluorene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 2-acetylaminofluorene may be collected and placed in an appropriate container.
3. For small quantities of liquids containing 2-acetylaminofluorene, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing 2-acetylaminofluorene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. 2-acetylaminofluorene dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container. Dry sweeping and dry mopping of 2-acetylaminofluorene are prohibited by OSHA.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 2-acetylaminofluorene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLONITRILE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about acrylonitrile for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C₃H₃
- **Structure:** $\text{CH}_2=\underset{\text{CN}}{\text{CH}}$
- **Synonyms:** Acrylon, AN, carbacryl, cyanoethylene, fumi-grain, propenenitrile, VCN, ventox, vinyl cyanide
- **Identifiers:** CAS 107-31-1; RTECS AT5250000; DOT 1093, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Pale yellow liquid with an unpleasant odor similar to pyridine

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 53.07
 2. Boiling point (at 760 mmHg): 77.3°C (171°F)
 3. Specific gravity at 20°C (68°C) (water = 1): 0.81
 4. Vapor density (air = 1 at boiling point of acrylonitrile): 1.83
 5. Melting point: -83°C (-117°F)
 6. Vapor pressure at 20°C (68°F): 83 mmHg
 7. Solubility in water, g/100 g water at 20°C (68°F): 7.35
 8. Evaporation rate (butyl acetate = 1): 4.54
 9. Saturation concentration in air (approximate) at 20°C (68°F): 10.9% (109,000 ppm)
 10. Ionization potential: 10.91 eV
- **Reactivity**
 1. Incompatibilities: Contact with strong oxidizers, especially bromine, and strong bases may cause fires and explosions. Contact with copper, copper alloys, ammonia, or amines may cause decomposition. Acrylonitrile will polymerize when hot, and the additional heat liberated by the polymerization may

generate high internal pressure and cause containers to explode. Inhibitors are added to the commercial product to prevent self-polymerization.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving acrylonitrile.

3. Caution: Acrylonitrile will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -1°C (30°F) (closed cup)
2. Autoignition temperature: 481°C (898°F)
3. Flammable limits in air, % by volume: Lower, 3; Upper, 17
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: Approximately 20 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylonitrile is 2 parts of acrylonitrile per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the OSHA ceiling concentration which shall at no time be exceeded is 10 ppm as determined in any 15-minute sampling period (Skin). The notation for "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that acrylonitrile be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 1 ppm as a TWA for up to an 8-hour workshift, 40-hour workweek; the NIOSH ceiling concentration is 10 ppm as determined in any 15-minute sampling period (Skin). The American Conference of Governmental In-

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dustrial Hygienists (ACGIH) has designated acrylonitrile as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV[®]) of 2 ppm [4.5 milligrams of acrylonitrile per cubic meter of air (4.5 mg/m³)] as a TWA for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational Exposure Limits for acrylonitrile

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA (Skin)*	2	—
Ceiling (15 min) (Skin)	10	—
NIOSH REL TWA (Skin) (Ca)†	1	—
Ceiling (15 min) (Skin)	10	—
ACGIH TLV [®] TWA (Skin) (A2)§	2	4.5

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Acrylonitrile may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* In rats, guinea pigs, or dogs, acute inhalation or oral administration of acrylonitrile caused signs of toxicity including decreased water and food consumption, decreased weight gain, histologic changes in the brain resembling anoxia, or damage to the lungs, liver, or kidneys. In rats, chronic inhalation or oral administration of acrylonitrile produced tumors of the brain, stomach, ear canal, and mammary glands, and cancer of the Zymbal gland. Oral administration of acrylonitrile to pregnant rats caused embryotoxic and teratogenic effects.

2. *Effects on humans:* Two separate studies of workers who were potentially exposed to acrylonitrile and who were observed over an 18- or 20-year period showed increased incidences of lung and colon cancers. In addition, at least two deaths from accidental inhalation or skin absorption of acrylonitrile have occurred.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to acrylonitrile can cause eye irritation, headache, sneezing, nausea, vomiting, weakness, light-headedness, and asphyxia.

2. *Long-term (chronic):* Skin contact with acrylonitrile can cause burns, blisters, and dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to acrylonitrile, the 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 skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to acrylonitrile at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis, and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

- **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to acrylonitrile. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to acrylonitrile may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to acrylonitrile should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of acrylonitrile. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure

detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting acrylonitrile vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure acrylonitrile may also be used if available. A detailed sampling and analytical method for acrylonitrile may be found in the *NIOSH Manual of Analytical Methods* (method number 1604).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with acrylonitrile.

SANITATION

Clothing which is contaminated with acrylonitrile should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of acrylonitrile from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of acrylonitrile's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with acrylonitrile should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle acrylonitrile should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to acrylonitrile may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for acrylonitrile

Operations	Controls
During use in the manufacture of ABS resin, SAN resin, plastic, or surface coating materials	Total enclosure
During the manufacture and transfer of monomer to other reaction vessels or to tank cars.	Total enclosure, local exhaust ventilation, personal protective equipment
During use as a chemical intermediate; during use in the cyanoethylation of cotton	Local exhaust ventilation, personal protective equipment
During use in surface coating applications	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to acrylonitrile, an eye-wash fountain should be provided within the immediate work area for emergency use.

If acrylonitrile gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to acrylonitrile, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If acrylonitrile gets on the skin, wash it immediately with soap and water. If acrylonitrile penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If acrylonitrile is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing acrylonitrile, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing acrylonitrile may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing acrylonitrile may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for acrylonitrile

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALDRIN POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

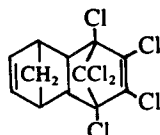
This guideline summarizes pertinent information about aldrin for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

NOTE: Most uses of aldrin were suspended by the U.S. Environmental Protection Agency, effective October 18, 1974. The only uses allowed are direct soil application, seed treatment if labeled "not for food use," dipping of plant roots and tops, subsurface termite control, and hot-caps.

SUBSTANCE IDENTIFICATION

• **Formula:** C₁₂H₈Cl₆

• **Structure:**



• **Synonyms:** Aldrex; aldrine; aldrosol; octalene; 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1,4-endo-5,8-dimethanonaphthalene

• **Identifiers:** CAS 309-00-2; RTECS 102100000; DOT 2761, label required: "Poison"

• **Appearance and odor:** Light to dark brown crystals with a mild chemical odor

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 364.90
2. Boiling point (at 760 mmHg): Decomposes
3. Specific gravity (water = 1): 1.6
4. Melting point: 104°C (219°F)

5. Vapor pressure at 20°C (68°F): 6.0 x 10⁻⁶ mmHg
6. Solubility in water: 0.027 mg/l at 27°C (80.6°F)

• **Reactivity**

1. Incompatibilities: Aldrin may react with concentrated mineral acids, acid catalysts, acid oxidizing agents, phenols, or reactive metals.
2. Hazardous decomposition products: Hydrochloric acid fumes and other chlorinated decomposition products may be released in a fire involving aldrin.
3. Caution: Aldrin should be stored in tightly closed containers in a well-ventilated area.

• **Flammability**

Aldrin is nonflammable.

• **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for aldrin is 0.25 milligrams of aldrin per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that aldrin be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.15 mg/m³ as a TWA for up to a 10-hour workshift, 40-hour workweek. The NIOSH REL is the lowest concentration detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 0.25 mg/m³ (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for aldrin

	Exposure limits mg/m ³
OSHA PEL TWA (Skin)*	0.25
NIOSH REL TWA (Ca)†	§0.15
ACGIH TLV® TWA (Skin)	0.25

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ Lowest reliably detectable level.

HEALTH HAZARD INFORMATION

• Routes of exposure

Aldrin may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact. Dermal absorption is substantially increased when aldrin is dissolved in organic solvents.

• Summary of toxicology

1. *Effects on animals*: Acute or chronic oral administration of aldrin to dogs and rats produced liver and kidney degeneration; chronic oral administration produced liver cancer in mice and thyroid cancer in rats. Aldrin fed to pregnant hamsters and mice caused increased fetal deaths, as well as congenital anomalies and growth retardation in the offspring.

2. *Effects on humans*: Aldrin is a neurotoxin and has caused electroencephalogram abnormalities following short-term or long-term oral, dermal, or inhalation exposure.

• Signs and symptoms of exposure

1. *Short-term (acute)*: Exposure to aldrin can cause hyperirritability, headache, dizziness, nausea, vomiting, blood in the urine, tremors, convulsions, and coma.

2. *Long-term (chronic)*: Exposure to aldrin can cause redness of the skin and dermatitis, weight loss, muscular twitching, and convulsions.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to aldrin, the 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, liver, kidneys, endocrine glands, and hematopoietic (blood-cell-forming), reproductive, and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to aldrin at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include: preexisting chronic diseases of the skin, liver, kidneys, endocrine glands, and hematopoietic, reproductive, and nervous systems. Workers should inform their physicians of their potential for exposures to aldrin because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter." The physician should obtain baseline values for liver function tests and a complete blood count with reticulocyte count.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to aldrin. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, eyes, liver, kidney, and hematopoietic, reproductive, and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to aldrin may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Non-autoimmune hemolytic anemia.
2. Delayed-onset SHE's include: Cataract, toxic hepatitis, and non-autoimmune hemolytic anemia.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to aldrin should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting aldrin with a glass-fiber filter and a midjet impinger containing iso-octane. The filter is extracted using iso-octane, and analysis is performed using a gas chromatograph with an electrolytic conductivity detector. A detailed sampling and analytical method for aldrin may be found in the *NIOSH Manual of Analytical Methods* (method number 5502).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with aldrin.

SANITATION

Clothing which is contaminated with aldrin should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of aldrin from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of aldrin's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with aldrin should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle aldrin should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to aldrin may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for aldrin

Operations	Controls
During formulation and handling of insecticide	Personal protective equipment, local exhaust ventilation
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to aldrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

If aldrin gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to aldrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If aldrin gets on the skin, wash it immediately with soap and water. If aldrin penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If aldrin is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Aldrin solid may be collected and placed in an appropriate container.
3. Aldrin solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system.
4. For small quantities of liquids containing aldrin, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing aldrin may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators,

requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for aldrin

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 4-AMINODIPHENYL POTENTIAL HUMAN CARCINOGEN

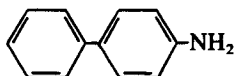
INTRODUCTION

This guideline summarizes pertinent information about 4-aminodiphenyl for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₁₂H₁₁N

• **Structure:**



• **Synonyms:** 4-ADP; p-aminodiphenyl; 4-aminobiphenyl; 4-biphenylamine; (1,1' -biphenyl)-4-amine; diphenylamine; p-phenylaniline; xenylamine

• **Identifiers:** CAS 92-67-1; RTECS DU8925000; DOT not assigned

• **Appearance and odor:** Colorless crystals with a floral odor which turn purple on contact with air

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 169.24
2. Boiling point (at 760 mmHg): 302 °C (575.6 °F)
3. Specific gravity (water = 1): 1.160
4. Vapor density (air = 1 at boiling point of 4-aminodiphenyl): 5.8
5. Melting point: 53 °C (177 °F)
6. Solubility in water, g/100 g water at 25 °C (77 °F): 0.18

• **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 4-aminodiphenyl.

• **Flammability**

1. Flash point: 152.7 °C (307 °F) (closed cup)
2. Autoignition temperature: 635 °C (1,175 °F)

3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide

4. Combustible solid, Flammability Rating 1 (NFPA)

• **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 4-aminodiphenyl; however, the OSHA standard requires implementation of stringent controls wherever 4-aminodiphenyl or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-aminodiphenyl are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1011, 4-Aminodiphenyl. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 4-aminodiphenyl as an A1 carcinogen (confirmed human carcinogen) (Skin). The "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. ACGIH recommends that virtually no exposure or contact by any route (i.e., respiratory, skin, or oral, as detected by the most sensitive methods) be permitted.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

4-Aminodiphenyl may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• **Summary of toxicology**

1. *Effects on animals:* In mice, subchronic or chronic subcutaneous injection or oral administration of 4-aminodiphenyl produced cancers of the liver, bladder, or mammary glands. Chronic oral administration of 4-aminodiphenyl to dogs caused salivation, loss of body weight, blood in the urine, and bladder cancer.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

2. *Effects on humans*: Chronic exposure of workers to 4-aminodiphenyl has been associated with an increased incidence of bladder cancer.

- **Signs and symptoms of exposure**

1. *Short-term (acute)*: Exposure to 4-aminodiphenyl can cause headache, lethargy, urinary tract burning, blood in the urine, and bluish discoloration of the skin and mucous membranes (due to methemoglobinemia).

2. *Long-term (chronic)*: Exposure to 4-aminodiphenyl can cause blood and pus in urine and frequent, painful urination.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 4-aminodiphenyl, the 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 liver and urinary tract.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 4-aminodiphenyl. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the con-

dition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 4-aminodiphenyl. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the liver and urinary tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The physician should consider use of a test which characterizes internal exposure (e.g., benzidine in urine). However, this test should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to 4-aminodiphenyl may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting 4-aminodiphenyl dust with glass fiber filters and silica gel tubes followed by elution with 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure 4-aminodiphenyl may also be used if available. A detailed sampling and analytical method for 4-aminodiphenyl may be found in the *NIOSH Manual of Analytical Methods* (method number 269).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe

covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting from a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 4-aminodiphenyl should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 4-aminodiphenyl from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-aminodiphenyl's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 4-aminodiphenyl from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1011:

Areas where 4-aminodiphenyl is manufactured, processed, used, repackaged, released, handled, or stored shall be desig-

nated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 4-aminodiphenyl, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 4-aminodiphenyl which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-aminodiphenyl into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 4-aminodiphenyl shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 4-aminodiphenyl from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-aminodiphenyl may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 4-aminodiphenyl

Operations	Controls
During use in research and laboratory facilities	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good house-keeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 4-aminodiphenyl, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to 4-aminodiphenyl, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-aminodiphenyl gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to 4-aminodiphenyl, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-aminodiphenyl gets on the skin, wash it immediately with soap and water. If 4-aminodiphenyl penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots,

and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 4-aminodiphenyl is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, 4-aminodiphenyl may be collected and placed in an appropriate container.
4. For small quantities of liquids containing 4-aminodiphenyl, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation.
5. Large quantities of liquids containing 4-aminodiphenyl may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
6. 4-Aminodiphenyl dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of 4-aminodiphenyl are prohibited by OSHA. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 4-aminodiphenyl

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ARSINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about arsine for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines. For information on other arsenic compounds, see guideline for inorganic arsenic.

SUBSTANCE IDENTIFICATION

- **Formula:** AsH₃
- **Synonyms:** Arsenic hydride, arsenic trihydride, hydrogen arsenide
- **Identifiers:** CAS 7784-42-1; RTECS CG6475000; DOT 2188, label required: "Poison, Flammable Gas"
- **Appearance and odor:** Colorless gas with a faint odor like garlic

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 77.95
 2. Boiling point (at 760 mmHg): -62.5°C (-80.5°F)
 3. Vapor density (air = 1 at boiling point of arsine): 2.69
 4. Melting point: -116°C (-177°F)
 5. Vapor pressure at 20°C (68°F): >1 atm
 6. Solubility in water, g/100 g water at 20°C (68°F): 0.07
 7. Ionization potential: 10.03 eV
- **Reactivity**
 1. Incompatibilities: Arsine reacts with strong oxidizers, especially chlorine and nitric acid. Arsine decomposes at temperatures above 300°C (572°F) to form elemental arsenic and hydrogen. In the presence of moisture, decomposition may be triggered by light.
 2. Hazardous decomposition products: Toxic fumes may be released in a fire involving arsine.

- **Flammability**

Flammable gas

- **Warning properties**

1. Odor threshold: 0.5 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for arsine is 0.05 parts of arsine per million parts of air (ppm) [0.2 milligrams of arsine per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that arsenic and all its inorganic compounds including arsine be regarded as potential human carcinogens in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) for arsine is 0.002 mg/m³ (as arsenic) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.05 ppm (0.2 mg/m³) for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for arsine

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	0.05	0.2
NIOSH REL (as arsenic) ceiling (15 min) (Ca)*	—	0.002
ACGIH TLV® TWA	0.05	0.2

* (Ca): NIOSH recommends treating as a potential human carcinogen.

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HEALTH HAZARD INFORMATION

• Routes of exposure

Arsine may cause adverse health effects following exposure via inhalation.

• Summary of toxicology

Effects on humans: Acute inhalation of arsine has caused the breakdown of red blood cells and hemoglobin, impairment of kidney function, damage to the liver and heart, electroencephalogram abnormality (elevation of T-waves), hemolytic anemia, and death due to kidney or heart failure. The human carcinogenic potential of arsine itself has not been determined; however, inorganic arsenic, a recognized human carcinogen in the workplace, is used in the production of arsine.

• Signs and symptoms of exposure

Short-term (acute): Exposure to arsine can cause the delayed onset of headache, malaise, weakness, dizziness, breathing difficulty (dyspnea), abdominal pain, nausea, vomiting, jaundice, bloody urine followed by absence of urination, pulmonary edema, and coma.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to arsine, the physician should evaluate and document the worker's baseline health status with thorough medical,

environmental, and occupational histories, a physical examination, and physiological and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, liver, kidneys, and lymphatic and hematopoietic (blood cell forming), respiratory, and peripheral nervous systems. A complete blood count with a reticulocyte count should be performed. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to arsine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or peripheral neuropathy, a history and other findings consistent with chronic disease of the skin or nervous system, and significant breathing impairment due to preexisting chronic lung disease.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to arsine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, kidneys, and hematopoietic, lymphatic, respiratory, and peripheral nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to arsine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

1. Acute SHE's include: Non-autoimmune hemolytic anemia and acute renal (kidney) failure
2. Delayed-onset SHE's include: Chronic renal (kidney) failure (see also SHE's for inorganic arsenic and its compounds)

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of arsine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by workers) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• Method

Sampling and analysis may be performed by collecting arsine using charcoal tubes with prefilters to capture particulates followed by desorption with nitric acid and analysis by atomic absorption spectrophotometry with heated graphite atomization. Direct-reading devices calibrated to measure arsine may also be used if available. A detailed sampling and analytical method for arsine may be found in the *NIOSH Manual of Analytical Methods* (method number 6001).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate clothing necessary to prevent skin contact with arsine.

SANITATION

Clothing which is contaminated with arsine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of arsine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of arsine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or smoking of tobacco or other

smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle arsine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

Contact lenses should not be worn when there is a potential for exposure to arsine.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to arsine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for arsine

Operations	Controls
During the manufacture of electrical semi-conductors and gallium arsenide; during the manufacture, storage, and distribution of arsine	Process enclosure, local exhaust ventilation, personal protective equipment
During the refining of metal ores that may contain arsenic	Local exhaust ventilation, personal protective equipment
During cleaning of metal equipment, electroplating of metals, metallic pickling, soldering and etching, photo-duplication, and use of photographic emulsions	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

If arsine is leaked, the following steps should be taken:

1. Stop the flow of arsine gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Ventilate area of leak.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are done in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning.

The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for arsine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted canister providing protection against the compound of concern Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ASBESTOS POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about asbestos for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for various forms of asbestos: (1) Asbestos (mixed forms);

- (2) Chrysotile;
- (3) Amosite;
- (4) Crocidolite;
- (5) Tremolite;
- (6) Anthophyllite;
- (7) Actinolite.

If unspecified, data apply to all forms.

- **Composition:** (1) Not Available;
- (2) $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$;
- (3) $(\text{FeMg})\text{SiO}_3$;
- (4) $\text{NaFe}(\text{SiO}_3)_2\cdot \text{FeSiO}_3\cdot \text{H}_2\text{O}$;
- (5) $\text{Ca}_2\text{Mg}_3\text{Si}_8\text{O}_{22}(\text{OH})_2$;
- (6) $(\text{MgFe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$;
- (7) $\text{CaO}\cdot 3(\text{MgFe})\text{O}\cdot 4\text{SiO}_2$
- **Synonyms:** (1) Asbestos fiber, serpentine, amphibole;
- (2) Canadian chrysotile, white asbestos, serpentine;
- (3) Brown asbestos, fibrous grunerite;
- (4) Blue asbestos;
- (5) Fibrous tremolite;
- (6) Azbolen asbestos;
- (7) Not available
- **Identifiers:** (1) CAS 1332-21-4; RTECS CI6475000; DOT 2212 (blue) 2590 (white);
- (2) CAS 12001-29-5; RTECS CI6478500; DOT 2590;
- (3) CAS 12172-73-5; RTECS CI6477000; DOT Not assigned;
- (4) CAS 12001-28-4, RTECS CI6479000; DOT 2212;

- (5) CAS 14567-73-8; RTECS CI6560000; DOT Not assigned;
- (6) CAS 17068-78-9; RTECS CI6478000; DOT Not assigned;
- (7) CAS 13768-00-8; RTECS CI6476000; DOT Not assigned

• **Appearance and odor:** A fiber or filament, asbestos may have a "fluffy" appearance. Colors may vary from white, gray, blue, brown, green or yellow. Positive identification requires microscopic examination.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: (2) 277.13; (5) 185.03
2. Specific gravity (water = 1): 2.5-3.0
3. Noncombustible solid

• Warning properties

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

Only asbestos fibers greater than 5 micrometers (μm) in length are considered for the following exposure limits. The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for asbestos is 0.2 fiber per cubic centimeter (cc) of air as a time-weighted average (TWA) concentration over an 8-hour workshift with an action level of 0.1 fiber/cc as an hour TWA. The National Institute for Occupational Safety and Health (NIOSH) recommends that asbestos be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.1 fiber/cc (in 40-liter air sample) as a TWA concentration for up to an 8-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated asbestos as an A1 substance (suspected human carcinogen, with an assigned threshold limit value/ TLV[®]) of 2 fibers/cc for chrysotile, 0.5 fiber/cc for amosite, 0.2 fiber/cc for crocidolite, and 2 fibers/cc for other forms, as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

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Table 1.—Occupational exposure limits for asbestos

	Exposure limits mg/m ³ *
OSHA PEL TWA	0.2
Action level	0.1
NIOSH REL TWA (Ca)†	0.1
ACGIH TLV® TWA (Ala)§	
Chrysotile	2.0
Amosite	0.5
Crocidolite	0.2
Other forms	2.0

* Fibers greater than 5 µm in length.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (Ala): Human carcinogen with an assigned TLV®.

HEALTH HAZARD INFORMATION

• Routes of exposure

Asbestos may cause adverse health effects following exposure via inhalation or ingestion.

• Summary of toxicology

1. *Effects on animals*: Single intrapleural injections of asbestos in rats, rabbits, and hamsters produced mesothelioma (cancer of the chest or abdominal linings). In rats, chronic inhalation or oral administration of asbestos produced cancers of the lungs, stomach, kidneys, liver, or mammary glands. All forms of asbestos were found to be carcinogenic in treated animals.

2. *Effects on humans*: Exposure to asbestos has been found to significantly increase the risks of contracting asbestosis, lung cancer, and mesothelioma.

• Signs and symptoms of exposure

1. *Short-term (acute)*: Exposure to asbestos can cause shortness of breath, chest or abdominal pain, and irritation of the skin and mucous membranes.

2. *Long-term (chronic)*: Exposure to asbestos can cause reduced pulmonary function, breathing difficulty, dry cough, broadening and thickening of the ends of the fingers, and bluish discoloration of the skin and mucous membranes.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental

and biologic monitoring, medical screening, and morbidity and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to asbestos, the 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 respiratory system using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to asbestos at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include cigarette smoking, preexisting asbestos-related disease, and significant breathing impairment due to preexisting chronic lung diseases. In addition to the medical interview and physical examination, the means to identify these conditions may include the methods recommended by NIOSH and ATS.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to asbestos. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory system as compared to the baseline status of the individual worker or to the expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, tests of lung function, and chest X-rays.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because

occupational exposure to asbestos may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include: Scarring of the lungs (asbestosis) and its lining (pleural fibrosis) and cancer of the lungs (bronchogenic lung cancer) and its lining (mesothelioma).

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to asbestos should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis for airborne asbestos may be performed by collecting asbestos fibers with membrane filters and analyzing by phase contrast microscopy. A detailed sampling and analytical method for asbestos may be found in the *NIOSH Manual of Analytical Methods* (method number 7400).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with asbestos.

SANITATION

Clothing which is contaminated with asbestos should be removed at the end of the work period and placed in nonreusable, impermeable containers for storage, transport, and disposal until it can be discarded or until provision is made for the removal of asbestos from the clothing. These containers should be marked "Asbestos-Contaminated Clothing" in easy-to-read letters. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of asbestos's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with asbestos should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle asbestos should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to asbestos may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for asbestos

Operations	Controls
During asbestos removal	Process enclosure, wet process (when possible), personal protective equipment
During the production of asbestos or the manufacture of products containing asbestos	Process enclosure, local exhaust ventilation, wet process (when possible), personal protective equipment
During the demolition of buildings	Water spray, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to asbestos, an eye wash fountain should be provided within the immediate work area for emergency use.

If asbestos gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this substance.

- **Skin exposure**

If asbestos gets on the skin, wash it immediately with soap and water.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If asbestos is spilled or leaked, the following steps should be taken:

Asbestos dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for asbestos

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZIDINE POTENTIAL HUMAN CARCINOGEN

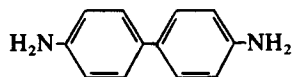
INTRODUCTION

This guideline summarizes pertinent information about benzidine for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₁₂H₁₂N₂

• **Structure:**



• **Synonyms:** 4,4'-Diaminobiphenyl; 4,4'-biphenyldiamine; 4,4'-diphenylenediamine; 4,4'-bianiline; p,p'-diaminobiphenyl; C.I. azoic diazo component 112; fast corinth base B

• **Identifiers:** CAS 92-87-5; RTECS DC9625000; DOT 1885, label required: "Poison"

• **Appearance and odor:** Colorless or slightly reddish crystalline compound that darkens on exposure to light and air

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 184.26
2. Boiling point (at 760 mmHg): 401.7°C (755°F)
3. Specific gravity (water = 1): 1.250
4. Vapor density (air = 1 at boiling point of benzidine): 6.36
5. Melting point: 129°C (264.2°F)
6. Solubility in water, g/100 g water at 12°C (53.6°F): 0.04

• **Reactivity**

Incompatibilities: Benzidine oxidizes on exposure to light and air.

• **Flammability**

Extinguishant: Dry chemical, alcohol foam, or carbon dioxide

• **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for benzidine; however, the OSHA standard requires implementation of stringent controls wherever benzidine or solid or liquid mixtures containing at least 0.1% by weight or volume of benzidine are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1010, Benzidine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated benzidine as an A1 substance (confirmed human carcinogen) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The ACGIH recommends that virtually no exposure or contact by any route (i.e., respiratory, skin, or oral, as detected by the most sensitive methods) be permitted.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Benzidine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

1. *Effects on animals:* Acute oral administration of benzidine to mice, rats, rabbits, and dogs produced loss of body weight, cloudy swelling and cirrhosis of the liver, degeneration of renal tubules, and hyperplasia of myeloid elements and lymphoid cells in the thymus and spleen. Subchronic or chronic subcutaneous injection, inhalation, or oral administration of benzidine to rats, mice, rabbits, or dogs produced cancers of the liver, bladder, intestine, lung, skin, and mammary or Zymbal glands.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

2. *Effects on humans*: Chronic exposure of workers to benzidine has been associated with an increased incidence of bladder cancer.

- **Signs and symptoms of exposure**

1. *Short-term (acute)*: Exposure to benzidine can cause shortness of breath, fatigue, bladder inflammation, and dermatitis.

2. *Long-term (chronic)*: Exposure to benzidine can cause blood in the urine and frequent, painful, or difficult urination.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to benzidine, the 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 risks. These should concentrate on the function and integrity of the skin, liver, urinary tract, and respiratory and hematopoietic (blood-cell-forming) systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to benzidine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and

degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to benzidine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, urinary tract, and respiratory and hematopoietic systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The physician should consider the use of a test that characterizes internal exposure (e.g., the presence of benzidine in urine). However, this test should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

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

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

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting benzidine dust with glass fiber filters and silica gel tubes followed by desorption with triethylamine in methanol and analysis by high pressure liquid chromatography with ultraviolet detection. Direct-reading devices calibrated to measure benzidine may also be used if applicable. A detailed sampling and analytical method for benzidine may be found in the *NIOSH Manual of Analytical Methods* (method number 5013).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where benzidine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting from a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where benzidine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower in designated areas after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with benzidine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of benzidine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of benzidine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove benzidine from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1010:

Areas where benzidine is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of benzidine, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving benzidine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of benzidine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where benzidine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of benzidine shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove benzidine from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzidine may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for benzidine

Operations	Controls
During use in the manufacture of azo dyes, as a hardener in the rubber industry, and in research and analytical laboratories for detection of blood and inorganics	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with benzidine, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to benzidine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If benzidine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to benzidine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If benzidine gets on the skin, wash it immediately with soap and water. If benzidine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If benzidine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, benzidine may be collected and placed in an appropriate container.
3. For small quantities of liquids containing benzidine, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing benzidine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Benzidine dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of benzidine are prohibited by OSHA.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforce-

ment and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for benzidine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

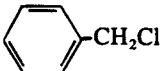
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about benzyl chloride for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₇H₇Cl

• **Structure:** 

- **Synonyms:** Alpha-chlorotoluene, chloromethylbenzene
- **Identifiers:** CAS 100-44-7; RTECS XS8925000; DOT 1738, label required: "Poison, Corrosive"
- **Appearance and odor:** Colorless to slightly yellow liquid with a pungent, aromatic, irritating odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 126.58
2. Boiling point (at 760 mmHg): 179.4°C (355°F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of benzyl chloride): 4.36
5. Melting point: -39.2°C (-38.6°F)
6. Vapor pressure at 22°C (71.6°F): 1 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.05
8. Evaporation rate (butyl acetate = 1): 0.11
9. Saturation concentration in air (approximate) at 22°C (71.6°F): 0.13% (1300 ppm)

• Reactivity

1. Incompatibilities: Contact with active metals such as copper, aluminum, magnesium, iron, zinc, and tin may cause the liberation of heat and hydrogen chloride. Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving benzyl chloride.

3. Caution: Benzyl chloride will attack some forms of plastic, rubber, and coatings.

• Flammability

1. Flash point: 67°C (153°F) (closed cup)
2. Autoignition temperature: 585°C (1085°F)
3. Flammable limits in air, % by volume: Lower, 1.1; Upper, Not available
4. Extinguishant: Dry chemical, foam, carbon dioxide, or water spray
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

• Warning properties

1. Odor threshold: 0.04 ppm
2. Eye irritation level: 16 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor and irritant effects, benzyl chloride can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzyl chloride is 1 part of benzyl chloride per million parts of air (ppm) [5 milligrams of benzyl chloride per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 1 ppm (5 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 1 ppm (5 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for benzyl chloride

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	1	5
NIOSH REL Ceiling (15 min)	1	5
ACGIH TLV [®] TWA	1	5

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• Routes of exposure

Benzyl chloride may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• Summary of toxicology

1. *Effects on animals*: Acute subcutaneous injection of benzyl chloride in rats caused labored breathing, bloody diarrhea, lung edema with bleeding, and liver damage. Acute inhalation of benzyl chloride by cats caused irregular respiration, inactivity, marked unresponsiveness, and death due to hemorrhage in the lungs; the surviving cats later developed clouded corneas, conjunctivitis, and severe pneumonia. Chronic subcutaneous injection of benzyl chloride in rats produced injection-site skin cancer and lung metastases. Oral administration of benzyl chloride to rats during pregnancy caused increased embryoletality and retarded postnatal development. NIOSH will continue to monitor the research regarding benzyl chloride to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.

2. *Effects on humans*: Long-term exposure of workers to benzyl chloride has caused increased incidences of respiratory illness and dermatitis, abnormal liver function and serum protein levels, and decreased white blood cell counts. An increased incidence of lung cancer has been reported for workers potentially exposed to benzyl and benzoyl chlorides.

• Signs and symptoms of exposure

Short-term (acute): Exposure to benzyl chloride can cause weakness, persistent headache, irritability, sweating, tremors, and loss of sleep and appetite. Skin sensitization, intense inflammation of the mucous membranes, and corneal damage can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on

an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to benzyl chloride, the 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 skin, eyes, liver, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to benzyl chloride at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to benzyl chloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, eyes, liver, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, tests of lung function, and chest X-rays.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to benzyl chloride may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of benzyl chloride. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• Method

Sampling and analysis may be performed by collecting benzyl chloride vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure benzyl chloride may also be used if available. A detailed sampling and analytical method for benzyl chloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1003).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with benzyl chloride.

Workers should be provided with and required to use splash-proof safety goggles where benzyl chloride may come in contact with the eyes.

SANITATION

Clothing which is contaminated with benzyl chloride should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of benzyl chloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of benzyl chloride's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with benzyl chloride should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the

storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle benzyl chloride should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzyl chloride may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for benzyl chloride

Operations	Controls
During use in the production of benzyl compounds	Process enclosure, local exhaust ventilation, personal protective equipment
During use in polymerization as a reactant catalyst, accelerator, and promoter; during use in rubber adhesives and TV tubes	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a raw material for pickling inhibitors, gasoline gum inhibitors, and synthetic tanning agents; during use in the processing of starch and the preparation of textile fibers	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to benzyl chloride, an eye-wash fountain should be provided within the immediate work area for emergency use. If benzyl chloride gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to benzyl chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If benzyl chloride gets on the skin, wash it immediately with soap and water. If benzyl chloride penetrates the clothing, re-

move the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If benzyl chloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing benzyl chloride, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from benzyl chloride vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing benzyl chloride may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Benzyl chloride should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing benzyl chloride may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and

Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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- Scientific Assembly on Environmental and Occupational Health: "Surveillance for Respiratory Hazards in the Occupational Setting," *American Review of Respiratory Diseases*, 126:952-956, 1982.

Table 3.—Respiratory protection for benzyl chloride

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 10 ppm	<p>Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)</p> <p>Any powered air-purifying respirator with organic vapor and acid gas cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)</p> <p>Any chemical cartridge respirator with organic vapor and acid gas cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)</p> <p>Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor and acid gas canister</p> <p>Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)</p>
Planned or emergency entry into environments containing unknown concentrations or levels above 10 ppm	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	<p>Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor and acid gas canister</p> <p>Any appropriate escape-type self-contained breathing apparatus</p>

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (5 mg/m³) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON BLACK POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about carbon black and carbon black containing polycyclic aromatic hydrocarbons (PAH's) for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Synonyms:** Channel black, furnace black, thermal black
- **Identifiers:** CAS 1333-86-4; RTECS FF5800000; DOT Not assigned
- **Appearance and odor:** Odorless black solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Specific gravity (water = 1): 1.8 to 2.18
 2. Vapor pressure at 20°C (68°F): Essentially zero
 3. Insoluble in water
- **Reactivity**
 1. Incompatibilities: Contact with strong oxidizers (e.g., chlorates, bromates, and nitrates) may cause fires and explosions.
 2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving carbon black.
 3. Caution: Carbon black dust may form explosive mixtures in air.
- **Flammability**
 1. Minimum dust ignition temperature: 510°C (950°F)
 2. Extinguishant: Water or carbon dioxide
 3. Combustible solid, (NFPA)
- **Warning properties**
 1. Evaluation of warning properties for respirator selection (carbon black): Based on lack of information on irritation levels, carbon black should be considered to have poor warning properties.
 2. Evaluation of warning properties for respirator selection (carbon black containing PAH's): Warning properties are not

considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbon black is 3.5 milligrams of carbon black per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for carbon black is 3.5 mg/m³ as a TWA for up to a 10-hour workshift, 40-hour workweek. NIOSH recommends that carbon black containing PAH's at a concentration greater than 0.1% be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH REL for PAH's that may be formed during the manufacture of carbon black and that could be adsorbed on the carbon black is 0.1 mg/m³ (measured as the cyclohexane-extractable fraction) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 3.5 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for carbon black

	Exposure limits mg/m ³
OSHA PEL TWA	3.5
NIOSH REL TWA (carbon black)	3.5
TWA (PAH's) (Ca)*	0.1
ACGIH TLV [®] TWA	3.5

* (Ca): NIOSH recommends treating as a potential human carcinogen when the concentration of PAH's is greater than 0.1%.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon black may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Summary of toxicology**

1. *Effects on animals:* Inhalation of carbon black by mice, rats, and monkeys caused thickened alveolar walls, increased pulmonary collagen, right atrial and ventricular strain, hypertrophy of the right and left ventricles and septum, and increased heart weights. Although carbon black itself did not cause cancer in treated animals, carbon black containing polynuclear hydrocarbons (PNA's) or PAH's did cause cancer following chronic administration by all routes tested.

2. *Effects on humans:* Chronic inhalation exposure of production workers has caused decreased pulmonary function and myocardial dystrophy. There is suggestive but inconclusive evidence that carbon black containing PAH's has been responsible for induction of skin cancer in exposed workers.

- **Signs and symptoms of exposure**

Long-term (chronic): Inhalation of carbon black can cause cough, phlegm, tiredness, chest pain, and headache. Dermal, mucosal, or inhalation exposure can cause irritation.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to carbon black, the 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 skin and respiratory system.

Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to carbon black at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to carbon black. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to carbon black may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to carbon black should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting carbon black particulate with tared 5 μ m PVC membrane filters and analyzing by gravimetric methods. A detailed sampling and analytical method for carbon black may be found in the *NIOSH Manual of Analytical Methods* (method number 5000). Sam-

pling and analysis of PAH's present in the particulate or the filters may be performed by extracting with cyclohexane (aided by sonification), filtering through a fritted glass funnel, and weighing a dried aliquot of the extract. A detailed sampling and analytical method for cyclohexane-extractable PAH's may be found in *Criteria for a Recommended Standard. . . Occupational Exposure to Carbon Black*.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with carbon black.

Workers should be provided with and required to use dust-proof safety goggles where carbon black may come in contact with the eyes.

SANITATION

Clothing which is contaminated with carbon black should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of carbon black from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of carbon black's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with carbon black should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle carbon black should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to carbon black may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for carbon black

Operations	Controls
During the manufacture of natural and synthetic rubber, dry cells, explosives, plastics, and paper	Local exhaust ventilation, personal protective equipment
During the manufacture and distribution of carbon black; during maintenance of equipment and storage containers	Local exhaust ventilation, personal protective equipment
During the manufacture and use of coatings and printing inks; during use as a coloring pigment and source of carbon	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to carbon black, an eye-wash fountain should be provided within the immediate work area for emergency use.

If carbon black gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to carbon black containing PAH's, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If carbon black gets on the skin, wash it immediately with soap and water. If carbon black penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If carbon black is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Carbon black dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it should then be placed in an appropriate container. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Tables 3 and 4).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed in Table 3. All respirators that have higher protection factors may also be used. Table 4 lists respirators for protection against carcinogens, which includes only those respirators providing the highest protection factor available.

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Table 3.—Respiratory protection for carbon black

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 17.5 mg/m ³	Any dust and mist respirator
Less than or equal to 35 mg/m ³	Any dust and mist respirator except single-use and quarter-mask respirators Any supplied-air respirator Any air-purifying respirator with a high-efficiency particulate filter Any self-contained breathing apparatus
Less than or equal to 87.5 mg/m ³	Any powered air-purifying respirator with a dust and mist filter Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 175 mg/m ³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 3,500 mg/m ³	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 3,500 mg/m ³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 3.5 mg/m³ (TWA).

Table 4.—Respiratory protection for carbon black containing greater than 0.1% PAH's

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROMETHYL METHYL ETHER POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about chloromethyl methyl ether for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C₂H₅ClO
- **Structure:** ClCH₂OCH₃
- **Synonyms:** Methyl chloromethyl ether, CMME, dimethylchloroether
- **Identifiers:** CAS 107-30-2; RTECS KN6650000; DOT 1239, label required: "Flammable Liquid"
- **Appearance:** Clear, colorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 80.52
 2. Boiling point (at 760 mmHg): 59.1°C (138.6°F)
 3. Specific gravity (water = 1): 1.0625
 4. Vapor density (air = 1 at boiling point of chloromethyl methyl ether): 2.77
 5. Melting point: -103.5°C (-154.3°F)
- **Reactivity**
 1. Incompatibilities: Chloromethyl methyl ether will react with surface moisture to evolve hydrogen chloride which is corrosive to metal.
 2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chloromethyl methyl ether.
 3. Caution: Technical grade chloromethyl methyl ether may contain 1-8% bis-chloromethyl ether, a potential human carcinogen. Chloromethyl methyl ether decomposes to hydrogen chloride and formaldehyde which can, under proper temperature and humidified conditions, form bis-chloromethyl ether.

- **Flammability**

1. Flash point: -17.8°C (0°F) (open cup)
2. Extinguishant: Dry chemical, foam, or carbon dioxide
3. Class IB Flammable Liquid (29 CFR 1910.106)

- **Warning properties**

1. Eye irritation levels: Chloromethyl methyl ether is severely irritating to the eyes and skin at 100 ppm.
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for chloromethyl methyl ether; however, the OSHA standard requires implementation of stringent controls wherever chloromethyl methyl ether or solid or liquid mixtures containing at least 0.1% by weight or volume of chloromethyl methyl ether are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1006, Methyl Chloromethyl Ether. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated chloromethyl methyl ether as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chloromethyl methyl ether may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Chronic subcutaneous injection of mice with chloromethyl methyl ether containing bis-chloromethyl ether produced skin cancer; chronic inhalation produced lung cancer.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

2. *Effects on humans*: Acute exposure to chloromethyl methyl ether vapor has caused corneal damage, pulmonary edema, pulmonary congestion, and pneumonia. Dermal exposure to liquid chloromethyl methyl ether has caused burns and tissue destruction (necrosis). Exposure to technical grade chloromethyl methyl ether, which is commonly contaminated with bis-chloromethyl ether (1-8%), has been associated with an increased incidence of lung cancer.

- **Signs and symptoms of exposure**

1. *Short-term (acute)*: Inhalation exposure to chloromethyl methyl ether can cause severe respiratory impairment, sore throat, fever, and chills. Chloromethyl methyl ether is also highly irritating to the mucous membranes, eyes, and skin.

2. *Long-term (chronic)*: Inhalation of chloromethyl methyl ether can cause coughing, wheezing, blood-stained sputum, breathing difficulty (dyspnea), and weight loss.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to chloromethyl methyl ether, the 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 skin and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods

recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to chloromethyl methyl ether at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to chloromethyl methyl ether. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to chloromethyl methyl ether may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Cancer of the respiratory tract (trachea, bronchi, and lungs).

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting chloromethyl methyl ether vapors with glass impingers followed by extraction with hexane and analysis by electron-capture gas chromatography. Direct-reading devices calibrated to measure chloromethyl methyl ether may also be used if applicable. A detailed sampling and analytical method for chloromethyl methyl ether may be found in the *NIOSH Manual of Analytical Methods* (method number 220).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the

manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with chloromethyl methyl ether should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of chloromethyl methyl ether from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of chloromethyl methyl ether's hazardous properties.

Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove chloromethyl methyl ether from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1006:

Areas where chloromethyl methyl ether is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of chloromethyl methyl ether, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving chloromethyl methyl ether which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of chloromethyl methyl ether into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of chloromethyl methyl ether shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove chloromethyl methyl ether from materials, equipment, and the decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to chloromethyl methyl ether may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for chloromethyl methyl ether

Operations	Controls
During use in the manufacture of ion-exchange resins and polymers; during use as a solvent for polymerization reactions and as a chloromethylation agent in chemical synthesis; during use in the treatment of textiles	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker had contact with chloromethyl methyl ether, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to chloromethyl methyl ether, an eye-wash fountain should be provided within the immediate work area for emergency use.

If chloromethyl methyl ether gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to chloromethyl methyl ether, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If chloromethyl methyl ether gets on the skin, wash it immediately with soap and water. If chloromethyl methyl ether penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If chloromethyl methyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing chloromethyl methyl ether, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing chloromethyl methyl ether may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing chloromethyl methyl ether may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for chloromethyl methyl ether

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR bis-CHLOROMETHYL ETHER POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about bis-chloromethyl ether for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C₂H₄Cl₂O
- **Structure:** ClCH₂OCH₂Cl
- **Synonyms:** bis(Chloromethyl) ether; bis-CME; chloro-(chloromethoxy) methane; chloromethyl ether; sym-dichlorodimethyl ether; sym-dichloromethyl ether; dimethyl-1'-dichloroether; oxybis(chloromethane)
- **Identifiers:** CAS 542-88-1; RTECS KN1575000; DOT 2249, label required: "Poison, Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a suffocating odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 114.96
 2. Boiling point (at 760 mmHg): 106°C (223°F)
 3. Specific gravity (water = 1): 1.315
 4. Vapor density (air = 1 at boiling point of bis-chloromethyl ether): 3.97
 5. Melting point: -41.5°C (-42.7°F)
- **Reactivity**
 1. Incompatibilities: bis-Chloromethyl ether is very volatile and may cause fire if exposed to excessive heat; bis-chloro-

methyl ether hydrolyzes in water to form hydrogen chloride and formaldehyde.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide, hydrogen chloride, and formaldehyde) may be released in a fire involving bis-chloromethyl ether.

3. Caution: Hydrogen chloride and formaldehyde react to form bis-chloromethyl ether under certain conditions of temperature and humidity. Any reaction in which these two compounds are present should be investigated for bis-chloromethyl ether formation.

- **Flammability**

Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for bis-chloromethyl ether; however, the OSHA standard requires implementation of stringent controls wherever bis-chloromethyl ether or solid or liquid mixtures containing at least 0.1% by weight or volume of bis-chloromethyl ether are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations 29 CFR 1910.1008, bis-Chloromethyl Ether. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated bis-chloromethyl ether as an A-1 substance (confirmed human carcinogen) having a TLV of 0.001 parts of bis-chloromethyl ether per million parts of air (ppm) [0.005 milligram per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• Routes of exposure

bis-Chloromethyl ether may cause adverse health effects following exposure via inhalation, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of bis-chloromethyl ether vapor by rats or hamsters caused pulmonary congestion, edema, and hemorrhage. Chronic inhalation of bis-chloromethyl ether by rats or mice produced cancers of the lungs, nasal cavity, or skin.

2. *Effects on humans:* Chronic inhalation of bis-chloromethyl ether has produced lung cancer and a reduction in pulmonary function.

• Signs and symptoms of exposure

1. *Short-term (acute):* bis-Chloromethyl ether vapor is highly irritating to the skin and eyes and to the mucous membranes of the respiratory tract. Liquid bis-chloromethyl ether can cause burns and tissue destruction (necrosis).

2. *Long-term (chronic):* Inhalation of bis-chloromethyl ether can cause breathing difficulty (dyspnea), wheezing, pulmonary hemorrhage, and increased bronchial secretions.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to bis-chloromethyl ether, the 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 skin and respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to bis-chloromethyl ether. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and lung dysfunction.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to bis-chloromethyl ether. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function. Because bis-chloromethyl ether is highly irritating to the skin and mucous membranes, the examining physician should be cognizant of any changes in the condition of the skin or signs of contact and/or allergic dermatitis.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to bis-chloromethyl ether may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

1. Acute SHE's include: Contact and/or allergic dermatitis
2. Delayed-onset SHE's include: Cancer of the trachea, bronchi, and lungs

MONITORING AND MEASUREMENT PROCEDURES

• Method

Sampling and analysis may be performed by collecting bis-chloromethyl ether vapors with Chromosorb 101 in short tubes followed by desorption with helium through a gas chromatographic column and analysis by mass spectroscopy. Direct-reading devices calibrated to measure bis-chloromethyl ether may also be used if available. Detailed sampling and analytical methods for bis-chloromethyl ether may be found in the *NIOSH Manual of Analytical Methods* (method numbers 213, 220).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory type hoods" or in locations where bis-chloromethyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where bis-chloromethyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with bis-chloromethyl ether should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision

is made for the removal of bis-chloromethyl ether from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of bis-chloromethyl ether's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove bis-chloromethyl ether from materials and equipment. Contaminated materials should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage of use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1008:

Areas where bis-chloromethyl ether is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of bis-chloromethyl ether, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving bis-chloromethyl ether which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of bis-chloromethyl ether into regulated areas, non-regulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where bis-chloromethyl ether is contained in an other-

wise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of bis-chloromethyl ether shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove bis-chloromethyl ether from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to bis-chloromethyl ether may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for bis-chloromethyl ether

Operations	Controls
During use in the manufacture of ion-exchange resins and polymers; during use as a solvent for polymerization reactions and as a chloromethylation agent in chemical synthesis; during use in the treatment of textiles	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with bis-chloromethyl ether, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to bis-chloromethyl ether, an eye-wash fountain should be provided within the immediate work area for emergency use.

If bis-chloromethyl ether gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to bis-chloromethyl ether, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If bis-chloromethyl ether gets on the skin, wash it immediately with soap and water. If bis-chloromethyl ether penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and before showering.

If bis-chloromethyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing bis-chloromethyl ether, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing bis-chloromethyl ether may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing bis-chloromethyl ether may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Any detectable concentration	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Planned or emergency entry into environments containing unknown or any detectable concentration	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Firefighting	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p>
Escape only	<p>Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister</p> <p>Any appropriate escape-type self-contained breathing apparatus</p>

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COTTON DUST

INTRODUCTION

This guideline summarizes pertinent information about cotton dust for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

"Cotton dust" is defined as dust generated into the atmosphere as a result of the processing of cotton fibers combined with any naturally occurring materials such as stems, leaves, bracts, and inorganic matter which may have accumulated on the cotton fibers during the growing or harvesting period. Any dust generated from the processing of cotton through the weaving of fabric in textile mills and dust generated in other operations or manufacturing processes using new or waste cotton fibers or cotton fiber by-products from textile mills is also considered cotton dust.

SUBSTANCE IDENTIFICATION

- **Identifiers:** RTECS GN2275000; DOT 1365 (cotton, wet or contaminated), label required: "Spontaneously Combustible"

- **Appearance:** Whitish solid (fibers and/or particulates)

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Specific gravity (water = 1): 1.3 (approximate)
2. Insoluble in water

- **Reactivity**

Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

- **Flammability**

1. Minimum ignition temperature: 470°C (878°F), cotton flock
2. Minimum explosive dust concentration: 0.05 g/L (50 g/m³), cotton flock
3. Extinguishant: Water
4. Combustible solid (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection:

Based on lack of information on odor threshold and eye irritation levels, cotton dust should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cotton dust is 200 micrograms of cotton dust per cubic meter of air ($\mu\text{g}/\text{m}^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift in yarn manufacturing and cotton washing operations; 750 $\mu\text{g}/\text{m}^3$ as a TWA over an 8-hour workshift in textile slashing and weaving operations; and 500 $\mu\text{g}/\text{m}^3$ as a TWA over an 8-hour workshift in textile mill waste house operations and dust from lower grade washed cotton in yarn manufacturing; and 1,000 $\mu\text{g}/\text{m}^3$ as a TWA over an 8-hour workshift in cotton waste processing operations of waste recycling (sorting, blending, cleaning, willowing, and garnetting). The National Institute for Occupational Safety and Health (NIOSH) recommends that exposure to cotton dust be reduced to the lowest feasible limit, which is defined as being a recommended exposure limit (REL) of less than 200 $\mu\text{g}/\text{m}^3$. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) for cotton dust (raw) is 200 $\mu\text{g}/\text{m}^3$ as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cotton dust

	Exposure limits $\mu\text{g}/\text{m}^3$
OSHA PEL TWA	200 (yarn manufacturing and cotton washing) 750 (slashing and weaving) 500 (textile mill waste house operations and lower grade washed cotton in yarn manufacturing)
	1,000 (waste recycling and garnetting)
NIOSH REL	<200
ACGIH TLV TWA	200

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HEALTH HAZARD INFORMATION

• Routes of exposure

Cotton dust may cause adverse health effects following exposure via inhalation.

• Summary of toxicology

1. *Effects on animals*: In rabbits, inhalation of cotton dust combined with bacterial (*Escherichia coli*) endotoxin caused bronchitis.

2. *Effects on humans*: Short-term exposure to cotton dust has caused bronchitis and acute byssinosis (also known as "Brown Lung" or "Monday Morning Fever"), a reversible respiratory disease produced by inhalation of cotton dust. Chronic exposure has caused lung airway obstruction (which reduces ventilatory capacity) and has led to disability and premature death. A direct relationship has been observed between the total concentration of cotton dust exposure and the rate of development of byssinosis. Among workers exposed to cotton dust, cigarette smokers have an increased risk of developing byssinosis. The biologically active material in cotton dust has not been ascertained; however, the risk of developing byssinosis appears to be reduced for workers who are exposed to dust from washed cotton.

• Signs and symptoms of exposure

1. *Short-term (acute)*: Exposure to cotton dust can produce a feeling of chest tightness, coughing, wheezing, phlegm, weakness, fever, chills, and breathing difficulty (dyspnea). These symptoms can disappear following removal from exposure (during brief periods away from work) and can reappear following reexposure.

2. *Long-term (chronic)*: Exposure to cotton dust can cause permanent and disabling breathing difficulties that include chronic bronchitis with emphysema.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to cotton dust should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from

results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to cotton dust, the 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 respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cotton dust at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or significant breathing impairment due to chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to cotton dust. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, pre- and post-shift tests of lung function, and chest X-rays.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to cotton dust may cause

diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Byssinosis (acute form)
2. Delayed-onset SHE's include: Byssinosis (chronic form) and chronic bronchitis with emphysema

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting cotton dust using a vertical elutriator preselector with a high-efficiency membrane filter and analyzing by gravimetric methods. Detailed sampling and analytical methods for cotton dust may be found in the *Criteria for a Recommended Standard . . . Occupational Exposure to Cotton Dust*.

SANITATION

Cleaning of equipment by "blowing-down" with compressed air or dry sweeping should be avoided. Vacuum cleaning should be instituted for all processes whenever possible. If "blow-down" is necessary, it should be conducted only in the absence of personnel not directly involved in the "blow-down" operation. Those workers involved in "blow-down" should wear adequate respiratory protection.

Good housekeeping practices designed to prevent the re-suspension of settled dust shall be developed and followed at all times.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cotton dust should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cotton dust may occur and control methods which may be effective in each case are listed in Table 2.

EMERGENCY FIRST AID PROCEDURES

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cotton dust, an eye-wash fountain should be provided within the immediate work area for emergency use. Contact lenses should not be worn when working with this substance.

Table 2.—Operations and methods of control for cotton dust

Operations	Controls
During carding operations, mixing and blowing operations, bale breaking, manufacturing of cotton yarn, and handling of cottonseed in the extraction of cottonseed oil	Process enclosure, local exhaust ventilation, personal protective equipment
During cotton batting operations and weaving of textiles containing cotton yarn	General dilution ventilation
During raw cotton ginning, bale pressing, and harvesting	Local exhaust ventilation, personal protective equipment

SPILLS AND LEAKS

In cases in which environmental levels exceed the NIOSH REL, workers not wearing respiratory protection should be restricted from areas of cotton dust contamination until cleanup has been completed.

If cotton dust contamination occurs, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of contamination.
3. Cotton dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container. If a vacuum system is used, there should be no sources of ignition in the vicinity of the contamination, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cotton dust

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 $\mu\text{g}/\text{m}^3$	Any dust respirator
Less than or equal to 2,000 $\mu\text{g}/\text{m}^3$	Any dust respirator except single-use and quarter-mask respirators Any supplied-air respirator Any air-purifying respirator with a high-efficiency particulate filter Any self-contained breathing apparatus
Less than or equal to 5,000 $\mu\text{g}/\text{m}^3$	Any powered air-purifying respirator with a dust filter Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 10,000 $\mu\text{g}/\text{m}^3$	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Planned or emergency entry into environments containing unknown concentrations or levels above 10,000 $\mu\text{g}/\text{m}^3$	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

*Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of <200 $\mu\text{g}/\text{m}^3$.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DDT POTENTIAL HUMAN CARCINOGEN

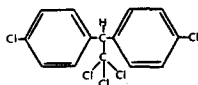
INTRODUCTION

This guideline summarizes pertinent information about DDT for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₁₄H₉Cl₅

• **Structure:**



- **Synonyms:** Citox; genitox; dichlorodiphenyltrichloroethane; 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
- **Identifiers:** CAS 50-29-3; RTECS KJ3325000; DOT 2761
- **Appearance and odor:** Colorless crystals or white to slightly off-white powder with a slightly aromatic odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 354.48
2. Boiling point (at 760 mmHg): 260°C (500°F)
3. Specific gravity (water = 1): 1.56
4. Vapor density (air = 1 at boiling point of DDT): 12.2
5. Melting point: 105-109°C (221-228°F)
6. Vapor pressure at 20°C (68°F): 1.5 x 10⁻⁷ mmHg
7. Practically insoluble in water

• Reactivity

1. Incompatibilities: DDT should not be stored in iron containers; DDT should not be mixed with iron and aluminum salts or with alkaline materials. Temperatures greater than 100°C (212°F) may cause decomposition.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride) may be released in a fire involving DDT.

3. Caution: DDT should be stored in a tightly closed container in a well-ventilated area.

• Warning properties

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DDT is 1 milligram of DDT per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that DDT be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.5 mg/m³ as a TWA for up to a 10-hour workshift, 40-hour workweek. The NIOSH REL is the lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 1 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek; the short-term exposure limit (STEL) is 3 mg/m³ (Table 1).

Table 1.—Occupational exposure limits for DDT

	Exposure limits mg/m ³
OSHA PEL TWA (Skin)*	1
NIOSH REL TWA (CA)†	0.5§
ACGIH TLV [®] TWA	1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ Lowest reliably detectable level.

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NOTE: A general ban was ordered by the Environmental Protection Agency on the registration of DDT, effective December 31, 1972. Effective the same date, the ban for uses of DDT by public health officials in disease control programs and by USDA and the military for health quarantine and prescription drugs use was lifted.

HEALTH HAZARD INFORMATION

• Routes of exposure

DDT may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

Effects on animals: Acute oral administration of DDT to rats caused tissue destruction (necrosis) of the liver, mild degeneration of kidney tubules, and changes in electroencephalograms. Chronic oral administration of DDT caused decreased fertility in rats and increased mortality of their offspring, toxic effects on the liver (including necrosis, fat deposition, increased weight, and increased enzyme activity), and liver cancer. In mice, chronic oral administration of DDT produced cancers of the liver, lungs, and lymphatic system.

• Signs and symptoms of exposure

Short-term (acute): Exposure to DDT can cause a prickling sensation of the tongue, lips, and face, a general feeling of ill health, headache, fatigue, vomiting, dizziness, tremors, convulsions, partial paralysis of the hands, and coma. DDT can also cause irritation of the eyes and skin.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to DDT, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic or laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, and reproductive and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DDT at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic liver disease. Workers should inform their physicians of their potential for exposures to DDT because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter."

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DDT. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, and reproductive and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to DDT may cause adverse reproductive effects or diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to DDT should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting DDT vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure DDT may also be used if available. A detailed sampling and analytical method for DDT may be found in the *NIOSH Manual of Analytical Methods* (method number S 274).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with DDT.

SANITATION

Clothing which is contaminated with DDT should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DDT from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DDT's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with DDT should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DDT should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DDT may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for DDT

Operations	Controls
During preparation and handling of insecticide	Process enclosure, local exhaust ventilation, personal protective equipment
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to DDT, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DDT gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to DDT, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DDT gets on the skin, wash it immediately with soap and water. If DDT penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DDT is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing DDT, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing DDT may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. If in solid form, DDT may be collected and placed in an appropriate container.
5. DDT dust may be collected by vacuuming with an appropriate high-efficiency filtration system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or

minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for DDT

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIELDRIN POTENTIAL HUMAN CARCINOGEN

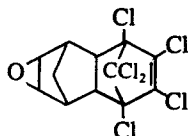
INTRODUCTION

This guideline summarizes pertinent information about dieldrin for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₁₂H₈Cl₆O

• **Structure:**



• **Synonyms:** Dieldrex; dieldrine; 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro,endo,exo-1,4:5,8-dimethanonaphthalene; illoxol; octalox

• **Identifiers:** CAS 60-57-1; RTECS IO1750000; DOT 2761

• **Appearance and odor:** Light brown crystals with a mild chemical odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 380.90
2. Boiling point (at 760 mmHg): Decomposes
3. Specific gravity (water = 1): 1.75
4. Vapor density (air = 1 at boiling point of dieldrin): 13.2
5. Melting point: 176°C (349°F)
6. Vapor pressure at 20°C (68°F): 1.8 x 10⁻⁷ mmHg
7. Solubility in water, mg/l water at 25°-29°C (77°-84°F): 0.186

• Reactivity

1. Incompatibilities: Dieldrin may react with concentrated mineral acids, acid catalysts, acid oxidizing agents, phenols, or reactive metals.
2. Hazardous decomposition products: Hydrochloric acid fumes and other chlorinated decomposition products may be released in a fire involving dieldrin.
3. Caution: Dieldrin should be stored in a tightly closed container in a well-ventilated area.

• Flammability

Nonflammable

• Warning properties

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for dieldrin is 0.25 milligrams of dieldrin per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour work-shift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that dieldrin be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.15 mg/m³ as a TWA for up to a 10-hour work-shift, 40-hour workweek. The NIOSH REL is the lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 0.25 mg/m³ (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for dieldrin

	Exposure limits mg/m ³
OSHA PEL TWA (Skin)*	0.25
NIOSH REL TWA (Ca)†	0.15§
ACGIH TLV [®] (Skin)	0.25

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ Lowest reliably detectable level.

NOTE: Most uses of dieldrin were suspended by the Environmental Protection Agency, effective October 18, 1974. The only

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

uses allowed are direct soil application, seed treatment if labeled "not for food use," dipping of plant roots and tops, sub-surface termite control, and hot-caps.

HEALTH HAZARD

• Routes of exposure

Dieldrin may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact. Dermal absorption is substantially increased when dieldrin is dissolved in organic solvents.

• Summary of toxicology

1. *Effects on animals:* Acute oral administration of dieldrin to rats caused liver and kidney degeneration. Chronic oral administration of dieldrin produced enlarged livers and increased liver enzyme activities in mice and rats, liver and lung cancers in mice, and adrenal cancer in rats. Dieldrin fed to pregnant mice and hamsters caused increased fetal deaths, congenital anomalies, and growth retardation in the offspring.

2. *Effects on humans:* Dieldrin is a neurotoxin and may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to dieldrin can cause hyperirritability, headache, dizziness, nausea, vomiting, blood in the urine, tremors, convulsions, and coma.

2. *Long-term (chronic):* Exposure to dieldrin can cause dermatitis, weight loss, muscular twitching, and convulsions.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals,

potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to dieldrin, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic or laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, eyes, liver, kidneys, and hematopoietic (blood-cell-forming), reproductive, and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to dieldrin at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include: preexisting chronic diseases of the skin, liver, kidneys, and hematopoietic and reproductive systems. Workers should inform their physicians of their potential for exposures to dieldrin because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter." The physician should obtain baseline values for liver function tests and a complete blood count with a reticulocyte count.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to dieldrin. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and hematopoietic, reproductive, and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to dieldrin may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

1. Acute SHE's include: Non-autoimmune hemolytic anemia.
2. Delayed onset SHE's include: Cataract, toxic hepatitis, and non-autoimmune hemolytic anemia.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to dieldrin should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• Method

Sampling and analysis may be performed by collecting dieldrin with glass fiber filters followed by extraction with iso-octane and analysis by gas chromatography. A detailed sampling and analytical method for dieldrin may be found in the *NIOSH Manual of Analytical Methods* (method number S283).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with dieldrin.

SANITATION

Clothing which is contaminated with dieldrin should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of dieldrin from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of dieldrin's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with dieldrin should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle dieldrin should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to dieldrin may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for dieldrin

Operations	Controls
During formulation and handling of insecticide	Personal protective equipment, local exhaust ventilation
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to dieldrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

If dieldrin gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to dieldrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If dieldrin gets on the skin, wash it immediately with soap and water. If dieldrin penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If dieldrin is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Dieldrin solid may be collected and placed in an appropriate container.
3. Dieldrin dust may be collected by vacuuming with an appropriate high-efficiency filtration system.
4. For small quantities of liquids containing dieldrin, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing dieldrin may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for dieldrin

Condition	Minimum respiratory protection*
Any detectable concentration	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Planned or emergency entry into environments containing unknown or any detectable concentration	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	<p>Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter</p> <p>Any appropriate escape-type self-contained breathing apparatus</p>

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DI-2-ETHYLHEXYL PHTHALATE (DEHP) POTENTIAL HUMAN CARCINOGEN

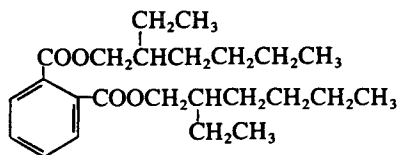
INTRODUCTION

This guideline summarizes pertinent information about di-2-ethylhexyl phthalate (DEHP) for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₂₄H₃₈O₄

• **Structure:**



• **Synonyms:** DEHP; 1,2-benzenedicarboxylic acid; bis(2-ethylhexyl) ester; bis(2-ethylhexyl) phthalate; DEHP; phthalic acid; bis(2-ethylhexyl) ester; di-sec octyl phthalate

• **Identifiers:** CAS 117-81-7; RTECS TI0350000; DOT not assigned

• **Appearance and odor:** Clear to slightly colored, oily, odorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 390.54
2. Boiling point (at 760 mmHg): 386 °C (727 °F)
3. Specific gravity (water = 1): 0.9861
4. Vapor density (air = 1 at boiling point of DEHP): 16
5. Melting point: -50 °C (-58 °F)
6. Vapor pressure: At 20 °C (68 °F), 0.01 mmHg; at 200 °C (392 °F), 1.32 mmHg
7. Solubility in water, g/100 g water at 20 °C (68 °F): 0.005
8. Evaporation rate (butyl acetate = 1): Almost zero

• **Reactivity**

1. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalis, or strong acids may cause fire and explosion.
2. Hazardous decomposition products: Toxic vapors and gases

(e.g., carbon monoxide) may be released in a fire involving DEHP.

• **Flammability**

1. Flash point: 218 °C (425 °F) (open cup)
2. Autoignition temperature: 390 °C (735 °F)
3. Flammable limits in air, % by volume: Lower, 0.3 at 245 °C (474 °F); Upper, Not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIB Combustible Liquid (29 CFR 1910.106), Flammability Rating 1 (NFPA)

• **Warning properties**

1. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DEHP is 5 milligrams of DEHP per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that DEHP be controlled and handled as a potential human carcinogen in the workplace, and the recommended exposure limit (REL) is that exposure be reduced to the lowest feasible limit. The use of DEHP in the quantitative fit testing of respirators should be discontinued and replaced with less toxic material such as refined corn oil. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 5 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 10 mg/m³ (Table 1).

Table 1.—Occupational exposure limits for di-2-ethylhexyl phthalate

	Exposure limits mg/m ³
OSHA PEL TWA	5
NIOSH REL (Ca)*	Lowest feasible limit
ACGIH TLV [®] TWA	5
STEL	10

* (Ca): NIOSH recommends treating as a potential human carcinogen.

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HEALTH HAZARD INFORMATION

• Routes of exposure

DEHP may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

Effects on animals: Subchronic inhalation of DEHP by rats or mice caused pulmonary irritation, swelling, and congestion of the liver and kidneys, renal cysts, bladder stones, testicular degeneration, increased liver metabolism and liver and kidney weights, and reduced weight gain, renal concentration capacity, blood hematocrit, and cholesterol and triglyceride levels. Chronic inhalation of DEHP by mice or rats produced liver cancer. Oral administration of DEHP to mice or rats on various days during fetal development caused a reduction in implantation rates, an increase in embryoletality, delayed births, and malformations of the skeletal system and the external and central nervous systems. Two-generation reproduction studies in treated rats showed a depression in placental and fetal weights and an increase in liver and kidney weights.

• Signs and symptoms of exposure

Short-term (acute): Exposure to DEHP can cause gastric disturbances and diarrhea. Skin sensitization and irritation of the eyes, skin, and respiratory tract can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure

to DEHP, the 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, liver, kidneys, gastrointestinal tract, and reproductive and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DEHP. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver or skin. The physician should obtain baseline values for liver function tests.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DEHP. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, gastrointestinal tract, and reproductive and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and lung function tests.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to DEHP may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

Acute SHE's include contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• Method

Sampling and analysis may be performed by collecting DEHP vapors with cellulose membrane filters followed by elution with

carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure DEHP may also be used if available. A detailed sampling and analytical method for DEHP may be found in the *NIOSH Manual of Analytical Methods* (method number 5020).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with DEHP.

SANITATION

Clothing which is contaminated with DEHP should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DEHP from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DEHP's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with DEHP should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DEHP should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DEHP may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for di-2-ethylhexyl phthalate (DEHP)

Operations	Controls
During bulk processing and application of plasticized polyvinyl chloride, polyvinylidene chloride, and other vinyl resins	Local exhaust ventilation, personal protective equipment
During hot processing of some plasticized polystyrenes, acrylics, urethanes, polyamides, and other synthetic resins	Local exhaust ventilation, personal protective equipment
During hot compounding plasticization of chlorinated rubbers and nitrile and neoprene rubbers	Local exhaust ventilation, personal protective equipment
During the application of nitrocellulose-based adhesives	Local exhaust ventilation, personal protective equipment
During hot esterification and subsequent steps in the manufacturing of DEHP	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to DEHP, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DEHP gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to DEHP, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DEHP gets on the skin, wash it immediately with soap and water. If DEHP penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DEHP is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing DEHP, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing DEHP may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing DEHP may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for di-2-ethylhexyl phthalate (DEHP)

Condition	Minimum respiratory protection*
Any detectable concentration	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 4-DIMETHYLAMINOAZOBENZENE POTENTIAL HUMAN CARCINOGEN

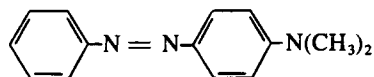
INTRODUCTION

This guideline summarizes pertinent information about 4-dimethylaminoazobenzene for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₁₄H₁₅N₃

• **Structure:**



• **Synonyms:** N,N-Dimethyl-4-aminoazobenzene; N,N-dimethyl-4-(phenylazo)-benzenamine; p-dimethylaminoazobenzene; N,N-dimethyl-p-phenylazoaniline; benzeneazodimethylaniline; methyl yellow; DAB

• **Identifiers:** CAS 60-11-7; RTECS BX7350000; DOT not assigned.

• **Appearance:** Yellow leaf-shaped crystals

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 225.32
2. Boiling point (at 760 mmHg): Sublimes
3. Vapor density (air = 1 at boiling point of 4-dimethylaminoazobenzene): 7.78
4. Melting point: 116 °C (240 °F)
5. Vapor pressure: Negligible
6. Insoluble in water

• **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 4-dimethylaminoazobenzene.

• **Flammability**

Extinguishant: Alcohol foam, carbon dioxide, or dry chemical

• **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 4-dimethylaminoazobenzene; however, the OSHA standard requires implementation of stringent controls wherever 4-dimethylaminoazobenzene or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-dimethylaminoazobenzene are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1015, 4-Dimethylaminoazobenzene. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have a threshold limit value (TLV®) for 4-dimethylaminoazobenzene.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

4-Dimethylaminoazobenzene may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• **Summary of toxicology**

Effects on animals: Acute or oral administration of 4-dimethylaminoazobenzene to rats caused liver degeneration. Subchronic and chronic intraperitoneal injection or oral administration of 4-dimethylaminoazobenzene to rats produced liver cirrhosis and cancer, and chronic dermal exposure produced skin cancer. Chronic oral administration of 4-dimethylaminoazobenzene to dogs produced bladder cancer. 4-Dimethylaminoazobenzene has been reported to cause skeletal defects in mice when administered at single doses during embryogenesis and also to cause the production of abnormal sperm in mice.

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- **Signs and symptoms of exposure**

Long-term (chronic): Exposure to 4-dimethylaminoazobenzene can cause contact dermatitis, weakness, dizziness, a feeling of euphoria, shortness of breath, irregular muscular action, and a bluish discoloration of skin and mucous membranes (due to methemoglobinemia).

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 4-dimethylaminoazobenzene, the 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 liver, skin, and urinary tract.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 4-dimethylaminoazobenzene.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin

or liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 4-dimethylaminoazobenzene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the liver, skin, and urinary tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to 4-dimethylaminoazobenzene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

- **Sentinel health events**

Acute and delayed-onset SHE's include: methemoglobinemia.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting 4-dimethylaminoazobenzene dust with glass-fiber filters and Gas-Chrom P sorbent followed by elution with 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure 4-dimethylaminoazobenzene may also be used if available. A detailed sampling and analytical method for 4-dimethylaminoazobenzene may be found in the *NIOSH Manual of Analytical Methods* (method number 284).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where 4-dimethylaminoazobenzene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and

equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 4-dimethylaminoazobenzene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 4-dimethylaminoazobenzene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 4-dimethylaminoazobenzene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-dimethylaminoazobenzene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 4-dimethylaminoazobenzene from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1015:

Areas where 4-dimethylaminoazobenzene is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from

these areas shall be restricted and controlled. Only authorized workers are permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 4-dimethylaminoazobenzene, including local and systemic toxicity, the specific nature of the operations which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 4-dimethylaminoazobenzene which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-dimethylaminoazobenzene into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-dimethylaminoazobenzene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 4-dimethylaminoazobenzene shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 4-dimethylaminoazobenzene from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-dimethylaminoazobenzene may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 4-dimethylaminoazobenzene

Operations	Controls
During use in research and laboratory facilities; during use as a coloring agent for polishes, waxes, polystyrene, petroleum, and soap	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 4-dimethylaminoazobenzene, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to 4-dimethylaminoazobenzene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-dimethylaminoazobenzene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to 4-dimethylaminoazobenzene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-dimethylaminoazobenzene gets on the skin, wash it immediately with soap and water. If 4-dimethylaminoazobenzene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 4-dimethylaminoazobenzene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 4-dimethylaminoazobenzene may be collected and placed in an appropriate container.
3. 4-Dimethylaminoazobenzene solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of 4-dimethylaminoazobenzene are prohibited by OSHA.
4. For small quantities of liquids containing 4-dimethylaminoazobenzene, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing 4-dimethylaminoazobenzene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators,

requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 4-dimethylaminoazobenzene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 1,1-DIMETHYLHYDRAZINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 1,1-dimethylhydrazine for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_2N_2H_8$
- **Structure:** $(CH_3)_2N-NH_2$
- **Synonyms:** Asymmetric dimethylhydrazine; dimazine; dimethylhydrazine; N,N-dimethylhydrazine; dimethylhydrazine unsymmetrical; DMH; UDMH
- **Identifiers:** CAS 157-14-7; RTECS MV2450000; DOT 1163, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid that fumes in air, gradually turns yellow, and has a fishy or ammonialike odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 60.12
 2. Boiling point (at 760 mmHg): 63.9°C (147°F)
 3. Specific gravity (water = 1): 0.782
 4. Vapor density (air = 1 at boiling point of 1,1-dimethylhydrazine): 2.08
 5. Melting point: -58°C (-72°F)
 6. Vapor pressure at 25°C (77°F): 156.8 mmHg
 7. Miscible with water
 8. Evaporation rate (butyl acetate = 1): 8.6
 9. Saturation concentration in air (approximate) at 25°C (77°F): 20.6% (206,000 ppm)
 10. Ionization potential: 7.46 eV
- **Reactivity**
 1. Incompatibilities: 1,1-dimethylhydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving 1,1-dimethylhydrazine.

3. Caution: 1, 1-Dimethylhydrazine will attack cork, some forms of plastics, coatings, and rubber.

• Flammability

1. Flash point: -15°C (5°F) (closed cup)
2. Autoignition temperature: 249°C (480°F)
3. Flammable limits in air, % by volume: Lower, 2; Upper, 95
4. Extinguishant: Alcohol foam, dry chemical, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Caution: 1,1-dimethylhydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

• Warning properties

1. Odor threshold: 6-14 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 1,1-dimethylhydrazine is 0.5 parts of 1,1-dimethylhydrazine per million parts of air (ppm) [1 milligram of 1,1-dimethylhydrazine per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that 1,1-dimethylhydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.06 ppm ($0.15 mg/m^3$) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Con-

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

ference of Governmental Industrial Hygienists (ACGIH) has designated 1,1-dimethylhydrazine as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 0.5 ppm (1.0 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for 1, 1-dimethylhydrazine

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA (Skin)*	0.5	1
NIOSH REL (Ca)† Ceiling (120 min)	0.06	0.15
ACGIH TLV® TWA (Skin) (A2)§	0.5	1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

1,1-Dimethylhydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of 1,1-dimethylhydrazine by mice, rats, or dogs caused central nervous system (CNS) stimulation, respiratory distress, convulsions, and death. Repeated daily exposure of dogs to 1,1-dimethylhydrazine vapor produced CNS depression, salivation, vomiting, diarrhea, loss of muscular coordination (ataxia), convulsive seizures, and hemolytic anemia. Chronic oral administration of 1,1-dimethylhydrazine to mice caused tumors of the blood vessels, lungs, kidneys, and liver.

2. *Effects on humans:* Exposure of workers to 1,1-dimethylhydrazine has caused increased blood pressure, fatty infiltration of the liver, impaired liver function (resulting in elevated serum glutamic-pyruvic transaminase levels, respiratory distress, hemolysis, and reduced oxygen supply to tissues (anoxia).

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure can cause a choking sensation, chest pain, breathing difficulty (dyspnea), lethargy, nausea, vomiting, and irritation of the skin, eyes, nose, and throat.

2. *Long-term (chronic):* Exposure to 1,1-dimethylhydrazine can cause pulmonary irritation, conjunctivitis, and gastrointestinal irritation.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease.

The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to 1,1-dimethylhydrazine, the 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, liver, kidneys, red blood cells, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis. A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 1,1-dimethylhydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to 1,1-dimethylhydrazine.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 1,1-dimethylhydrazine. The

interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, kidneys, red blood cells, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to 1,1-dimethylhydrazine may cause diseases of prolonged induction latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

Acute SHE's include contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of 1,1-dimethylhydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

Sampling and analysis may be performed by collecting 1,1-dimethylhydrazine vapors with sulfuric acid-coated silica gel tubes and analyzing by gas chromatography. Direct-reading devices calibrated to measure 1,1-dimethylhydrazine may also be used if available. A detailed sampling and analytical method for 1,1-dimethylhydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions. Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with 1,1-dimethylhydrazine.

SANITATION

Clothing which is contaminated with 1,1-dimethylhydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dimethylhydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 1,1-dimethylhydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with 1,1-dimethylhydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 1,1-dimethylhydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 1,1-dimethylhydrazine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 1, 1-dimethylhydrazine

Operations	Controls
During the formulation of and use in jet and rocket propellants	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture of 1,1-dimethylhydrazine and during maintenance of manufacturing and storage equipment	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the chemical synthesis of catalysts, automotive antifreeze, pharmaceuticals, dyestuffs, and stabilizing agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the formulation of photographic developers and the processing of styrene-butadiene rubber	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to 1,1-dimethylhydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 1,1-dimethylhydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to 1,1-dimethylhydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 1,1-dimethylhydrazine gets on the skin, wash it immediately with soap and water. If 1,1-dimethylhydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 1,1-dimethylhydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing 1,1-dimethylhydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing 1,1-dimethylhydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. 1,1-Dimethylhydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENE OXIDE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about ethylene oxide for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C₂H₄O



- **Synonyms:** Anprolene; dihydrooxirene; dimethylene oxide; EO; 1,2-epoxyethane; EtO; oxacyclopropane; oxane; oxiran; oxirane

- **Identifiers:** CAS 75-21-8; RTECS KX2450000; DOT 1040, label required: "Flammable Liquid"

- **Appearance and odor:** Colorless liquid or gas with an etherlike odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44.06
2. Boiling point (at 760 mmHg): 10.7°C (51.3°F)
3. Specific gravity (water = 1): 0.8711
4. Vapor density (air = 1 at boiling point of ethylene oxide): 1.5
5. Melting point: -111.3°C (-168°F)
6. Vapor pressure at 20°C (68°F): 1,095 mmHg
7. Soluble in water
8. Ionization potential: 10.56 eV

- **Reactivity**

1. Incompatibilities: Ethylene oxide reacts readily with alkali metal hydroxides or highly active catalysts (e.g., anhydrous

chlorides of iron, tin, or aluminum and oxides of iron or aluminum); ethylene oxide should not come in contact with copper.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving ethylene oxide.

3. Caution: Protect container against physical damage. Store in an outside area in insulated tanks or containers shielded from sun and heat. Ethylene oxide may interact with some plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -6°C (20°F) (open cup)
2. Autoignition temperature: 429°C (804°F)
3. Flammable limits in air, % by volume: Lower, 3; Upper, 100
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or water spray or fog
5. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)
6. All ignition sources, including static electricity, should be controlled. Flashback along a vapor trail may occur.

- **Warning properties**

1. Odor threshold: 430 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ethylene oxide is 1 part of ethylene oxide per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that ethylene oxide be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 5 ppm [9 milligrams per cubic meter (9 mg/m³)] as a ceiling concentration determined in any 10-minute sampling period and not to be achieved for more than 10 minutes dur-

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ing any workday. In addition, NIOSH recommends that exposure to ethylene oxide be less than 0.1 ppm (0.18 mg/m³) as a TWA for up to an 8-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated ethylene oxide as an A2 substance (suspected of carcinogenic potential for man) having an assigned threshold limit value (TLV[®]) of 1 ppm (2 mg/m³) as a TWA for a normal 8-hour workday and 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethylene oxide

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	1	—
NIOSH REL TWA (Ca)*	<0.1	<0.18
Ceiling (10 min/day)	5	9
ACGIH TLV [®] TWA (A2)†	1	2

* (Ca): NIOSH recommends treating as a potential human carcinogen.

† (A2): Suspected of carcinogenic potential for man.

HEALTH HAZARD INFORMATION

• Routes of exposure

Ethylene oxide may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of ethylene oxide by rats and guinea pigs caused pulmonary edema, paralysis, and corneal opacities. Subchronic inhalation of ethylene oxide by male and female rats prior to mating and during pregnancy caused a decrease in the number of pregnant females and in the number of offspring per litter. Chronic oral administration of ethylene oxide to rats produced cancer of the forestomach; chronic inhalation produced brain tumors, leukemia, and cancer of the peritoneum.

2. *Effects on humans:* Chronic exposure to ethylene oxide has caused anemia, peripheral neuropathy, and chromosomal damage in white blood cells (lymphocytes). Exposure to ethylene oxide has been associated with increased incidences of miscarriage, leukemia, and stomach cancer.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to ethylene oxide can cause nausea, headache, weakness, vomiting, drowsiness, incoordination, and irritation of the eyes, nose, throat, and lungs. Skin contact with ethylene oxide can cause blisters, edema, burns, frostbite, and severe dermatitis.

2. *Long-term (chronic):* Exposure to ethylene oxide can cause skin sensitization, numbing of the sense of smell, and respiratory infection.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to ethylene oxide, the 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, gastrointestinal tract, and hematopoietic (blood cell forming), nervous, reproductive, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to ethylene oxide at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis. In addition to a medical interview and physical examination, the physician should consider obtaining additional baseline electrophysiologic and electromyographic studies and an assess-

ment of fertility, using standardized methods and evaluation criteria.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to ethylene oxide. The interviews, examinations, and appropriate medical screening and/or biologic monitoring test should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, gastrointestinal tract, and hematopoietic, nervous, reproductive, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to ethylene oxide may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to ethylene oxide should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of ethylene oxide. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 10-minute sample or a series of consecutive samples that total 10 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used

as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting ethylene oxide vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure ethylene oxide may be used if available. A detailed sampling and analytical method for ethylene oxide may be found in the *NIOSH Manual of Analytical Methods* (method number 1607).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with liquid ethylene oxide.

SANITATION

Clothing which is contaminated with liquid ethylene oxide should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of ethylene oxide from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethylene oxide's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with ethylene oxide should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle ethylene oxide should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to ethylene oxide may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for ethylene oxide

Operations	Controls
During synthesis and handling of ethylene oxide	Process enclosure, local exhaust ventilation, personal protective equipment
During synthesis of ethylene glycols, glycol ethers, ethanalamines, amines, nonionic surface-active agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a sterilizing agent	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to ethylene oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethylene oxide gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to liquid ethylene oxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethylene oxide gets on the skin, wash it immediately with soap and water. If liquid ethylene oxide penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If ethylene oxide is spilled or leaked, the following steps should be taken:

1. If ethylene oxide is in the gaseous form, stop the flow of gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing ethylene oxide, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood duct work is free from ethylene oxide vapors. Burn the paper in a suitable location away from combustible materials.
5. Large quantities of liquids containing ethylene oxide may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Ethylene oxide should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
6. Liquids containing ethylene oxide may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134.

A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for ethylene oxide

Condition	Minimum respiratory protection*†
Concentration:	
Less than 5 ppm	Any air-purifying, full-facepiece canister respirator that provides protection against ethylene oxide and is equipped with an effective end-of-service-life indicator (ESLI) Any self-contained breathing apparatus equipped with a full facepiece Any supplied-air respirator with a full facepiece
Equal to or greater than 5 ppm, or planned or emergency entry into environments containing unknown concentrations	Any self-contained breathing apparatus equipped with a full facepiece and operated in a pressure-demand or positive-pressure mode Any supplied-air respirator equipped with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus equipped with a full facepiece and operated in a pressure-demand or other positive-pressure mode
Escape only	Any air-purifying, full-facepiece canister respirator that provides protection against ethylene oxide and is equipped with an effective ESLI Any appropriate escape-type, self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of <0.1 ppm (<0.18 mg/m³) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENE DICHLORIDE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about ethylene dichloride for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_2H_4Cl_2$
- **Structure:** $ClCH_2CH_2Cl$
- **Synonyms:** 1,2-Dichloroethane, dichloroethylene, ethane dichloride, ethylene chloride, glycol dichloride
- **Identifiers:** CAS 107-06-2; RTECS KI0525000; DOT 1184, label required: "Flammable Liquid"
- **Appearance and odor:** Clear, colorless, oily liquid with an odor like chloroform

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 98.96
 2. Boiling point (at 760 mmHg): 83.4°C (182°F)
 3. Specific gravity (water = 1): 1.253
 4. Vapor density (air = 1 at boiling point of ethylene dichloride): 3.42
 5. Melting point: -35.4°C (-31.7°F)
 6. Vapor pressure at 20°C (68°F): 68 mm Hg
 7. Solubility in water, g/100 g water at 20°C (68°F): 0.81
 8. Evaporation rate (butyl acetate = 1): 6.46
 9. Saturation concentration in air (approximate) at 25°C (77°F): 11.5% (115,000 ppm)
 10. Ionization potential: 11.04 eV
- **Reactivity**
 1. Incompatibilities: Strong oxidizers, strong caustics, or chemically active metals such as aluminum or magnesium powder, sodium, or potassium may cause fires and explosions.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving ethylene dichloride.

3. Caution: Ethylene dichloride is corrosive to iron and other metals unless it is stabilized with alkylamines. Ethylene dichloride will attack some forms of plastics and rubber.

• Flammability

1. Flash point: 13°C (55°F) (closed cup)
2. Autoignition temperature: 413°C (775°F)
3. Flammable limits in air, % by volume: Lower, 6.2; Upper, 15.9
4. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

• Warning properties

1. Odor threshold: 88 ppm
2. Eye irritation levels: 10 ppm
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ethylene dichloride is 50 parts of ethylene dichloride per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 100 ppm; and the maximum peak concentration above the acceptable ceiling concentration (maximum duration of 5 minutes in any 3 hours) is 200 ppm. The National Institute for Occupational Safety and Health (NIOSH) recommends that ethylene dichloride be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 1 ppm [4 milligrams of ethylene dichloride per cubic meter of air (mg/m^3)] as a TWA for up to a 10-hour workshift, 40-hour workweek; the NIOSH ceiling concentration is 2 ppm ($8 mg/m^3$) as determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 10 ppm

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(40 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethylene dichloride

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	50	—
Acceptable ceiling	100	—
Maximum ceiling (5 min in any 3 h)	200	—
NIOSH REL TWA (Ca)*	1	4
Ceiling (15 min)	2	8
ACGIH TLV® TWA	10	40

* (Ca): NIOSH recommends treating as a potential human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Ethylene dichloride may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Chronic inhalation or ingestion of ethylene dichloride by rats caused pulmonary tissue irritation, congestion, edema and pneumonia, degeneration of liver and kidney tissue, adrenal gland hemorrhage and cell damage, fatty infiltration and hemorrhage of cardiac tissue, and death due to respiratory or cardiac arrest. Cancers of the stomach, circulatory system, mammary glands, uterus, lungs, and skin were produced in similarly exposed rats and mice.

2. *Effects on humans:* Acute inhalation exposure to ethylene dichloride has caused respiratory tract irritation, congestion, edema and pneumonia, impaired functioning of the liver and kidneys, and myocardial hemorrhage. Chronic exposure has produced enlargement and fatty degeneration of the liver, impaired liver and kidney function, depression of nerve conduction, anemia, and increased serum bile salt levels. Ethylene dichloride has been detected in the milk of exposed lactating mothers.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to ethylene dichloride can cause headache, weakness, pain or irritation of the eyes and skin, bluish discoloration of skin and mucous membranes (cyanosis), nausea, vomiting, mental confusion, dizziness, incoordination, and unconsciousness.

2. *Long-term (chronic):* Exposure to ethylene dichloride can cause headache, fatigue, irritability, nervousness, cough, weakness, diarrhea, and muscle tremor. Severe irritation of the skin, edema, and tissue destruction (necrosis) can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to ethylene dichloride, the 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, liver, kidneys, and reproductive, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to ethylene dichloride at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that

may be attributed to exposure to ethylene dichloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and reproductive, cardiovascular, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to ethylene dichloride may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: None recognized (however, toxic hepatitis is a recognized SHE associated with occupational exposure to ethylene dibromide).

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to ethylene dichloride should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of ethylene dichloride. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis for ethylene dichloride may be performed by collecting ethylene dichloride vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure ethylene dichloride may also be used if available. A detailed sampling and analytical method for ethylene dichloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1003).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with ethylene dichloride.

SANITATION

Clothing which is contaminated with ethylene dichloride should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of ethylene dichloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethylene dichloride's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with ethylene dichloride should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle ethylene dichloride should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to ethylene dichloride may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for ethylene dichloride

Operations	Controls
During use as a chemical intermediate in the manufacture of vinyl chloride	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an intermediate in the production of chlorinated solvents and ethylenamines	Process enclosure, local exhaust ventilation, personal protective equipment
During the production of gasoline using tetraethyl lead as an anti-knock agent and ethylene dichloride as a lead scavenger	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a fumigant or industrial solvent	Local exhaust ventilation, personal protective equipment
During the manufacture of ethylene dichloride	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to ethylene dichloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethylene dichloride gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to ethylene dichloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethylene dichloride gets on the skin, wash it immediately with soap and water. If ethylene dichloride penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Un-

derstand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If ethylene dichloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing ethylene dichloride, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing ethylene dichloride may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing ethylene dichloride may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforce-

ment and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for ethylene dichloride

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

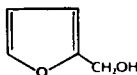
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR FURFURYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about furfuryl alcohol for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C₅H₆O₂
- **Structure:**



- **Synonyms:** 2-Furancarbinol, 2-furanmethanol, furfural alcohol, furyl alcohol, 2-furylcarbinol, 2-furylmethanol, 2-hydroxymethylfuran
- **Identifiers:** CAS 98-00-0; RTECS LU9100000; DOT 2874, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless to pale yellow, syrupy liquid with a mild odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 98.10
 2. Boiling point (at 760 mmHg): 170°C (338°F)
 3. Specific gravity (water = 1): 1.1351
 4. Vapor density (air = 1 at boiling point of furfuryl alcohol): 3.38
 5. Melting point: -14.63°C (5.7°F)
 6. Vapor pressure at 31.8°C (89°F): 1 mmHg
 7. Miscible with water
 8. Evaporation rate (butyl acetate = 1): Very slow
 9. Saturation concentration in air (approximate) at 31.8°C (89°F): 0.13% (1,300 ppm)
- **Reactivity**
 1. Incompatibilities: Contact with strong acids (including some organic acids) or acid catalysts may cause polymerization with

the liberation of heat and violent spattering. Avoid contact with strong oxidizers.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving furfuryl alcohol.

3. Caution: Furfuryl alcohol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 77°C (170°F) (closed cup)
2. Autoignition temperature: 490°C (915°F)
3. Flammable limits in air, % by volume: Lower, 1.8; Upper, 16.3
4. Extinguishant: Alcohol foam, carbon dioxide, or dry chemical
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 7-8 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, furfuryl alcohol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, furfuryl alcohol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for furfuryl alcohol is 50 parts of furfuryl alcohol per million parts of air (ppm) [200 milligrams of furfuryl alcohol per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 50 ppm (200 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 10 ppm (40 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek; and the ACGIH short-term exposure limit (STEL) is 15 ppm (60 mg/m³) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for furfuryl alcohol

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	50	200
NIOSH REL TWA	50	200
ACGIH TLV [®] TWA (Skin)*	10	40
STEL (Skin)	15	60

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• Routes of exposure

Furfuryl alcohol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of Toxicology

Effects on animals: Repeated daily exposure to mice, rats, or rabbits to furfuryl alcohol caused increased respiration, respiratory tract irritation, and vascular congestion, followed by decreased respiration, decreased force of cardiac contraction, decreased contractility of the gastrointestinal tract, drop in blood pressure, paralysis of sensory nerves, and death due to respiratory failure or possibly to cardiac arrest.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to furfuryl alcohol can cause excitement, drowsiness, nausea, vomiting, salivation, diarrhea, dizziness, shortness of breath, irregular breathing, and increased urination. Eye contact with furfuryl alcohol can cause redness, tearing, serious irritation, and corneal opacities; dermal contact can cause minor irritation.

2. *Long-term (chronic):* Exposure to furfuryl alcohol can cause headache, eye irritation, and dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evalu-

ated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to furfuryl alcohol, the 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, cardiovascular, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to furfuryl alcohol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to furfuryl alcohol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and cardiovascular, nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to furfuryl alcohol should be taken so that the TWA exposure is based on

a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting furfuryl alcohol vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure furfuryl alcohol may also be used if available. A detailed sampling and analytical method for furfuryl alcohol may be found in the *NIOSH Manual of Analytical Methods* (method number S365).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with furfuryl alcohol.

Workers should be provided with and required to use splash-proof safety goggles where furfuryl alcohol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with furfuryl alcohol should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of furfuryl alcohol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of furfuryl alcohol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with furfuryl alcohol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle furfuryl alcohol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to furfuryl alcohol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for furfuryl alcohol

Operations	Controls
During the manufacture of cements, molded high-density carbon, and graphite articles; during the preparation of furfuryl-dimethylol urea and furan resins	Local exhaust ventilation, general exhaust ventilation, personal protective equipment
During the synthesis and handling of furfuryl alcohol; during use as a solvent; during use in impregnation of wood	Local exhaust ventilation, general exhaust ventilation, personal protective equipment
During use in sand consolidation for oil and gas recovery operations	General dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to furfuryl alcohol, an eye-wash fountain should be provided within the immediate work area for emergency use.

If furfuryl alcohol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to furfuryl alcohol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If furfuryl alcohol gets on the skin, wash it immediately with soap and water. If furfuryl alcohol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If furfuryl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. For small quantities of liquids containing furfuryl alcohol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from furfuryl alcohol vapors. Burn the paper in a suitable location away from combustible materials.

4. Large quantities of liquids containing furfuryl alcohol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Furfuryl alcohol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for furfuryl alcohol

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 250 ppm	<p>Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)</p> <p>Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)</p> <p>Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)</p> <p>Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)</p>
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	<p>Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister</p> <p>Any appropriate escape-type self-contained breathing apparatus</p>

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 50 ppm (200 mg/m³) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR HYDRAZINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about hydrazine for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** N_2H_4
- **Structure:** H_2N-NH_2
- **Synonyms:** Diamide, diamine, hydrazine base, hydrazine anhydrous
- **Identifiers:** CAS 302-01-2; RTECS MU7175000; DOT 2029, label required: "Flammable Liquid and Poison"
- **Appearance and odor:** Colorless oily liquid that fumes in air and has a fishy or ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 32.06
 2. Boiling point (at 760 mmHg): 113.5°C (236°F)
 3. Specific gravity (water = 1): 1.004
 4. Vapor density (air = 1 at boiling point of hydrazine): 1.04
 5. Melting point: 1.4°C (34°F)
 6. Vapor pressure at 25°C (77°F): 14.4 mmHg
 7. Miscible with water
 8. Evaporation rate (butyl acetate = 1): 0.42
 9. Saturation concentration in air (approximate) at 25°C (77°F): 1.89% (18,900 ppm)
 10. Ionization potential: 8.36 eV
- **Reactivity**
 1. Incompatibilities: Hydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving hydrazine.

3. Caution: Hydrazine will attack cork and some forms of plastic, coatings, and rubber.

- **Flammability**

1. Flash point: 37.7°C (100°F) (closed cup)
2. Autoignition temperature: 24°C (75.2°F) on iron rust surface, 270°C (518°F) on glass surface
3. Flammable limits in air, % by volume: Lower, 4.7; Upper, 98
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Caution: Hydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

Odor threshold: 3-4 ppm

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hydrazine is 1.0 part of hydrazine per million parts of air (ppm) [1.3 milligrams of hydrazine per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that hydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.03 ppm ($0.04 mg/m^3$) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienist (ACGIH) has designated hydrazine as an A2 substance (suspected human carcinogen) having as assigned threshold limit value (TLV[®]) of 0.1 ppm (0.1 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for hydrazine

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA (Skin)*	1.0	1.3
NIOSH REL (Ca)†		
Ceiling (120 min)	0.03	0.04
ACGIH TLV [®] (A2)§		
TWA (Skin)	0.1	0.1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Hydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals*: Acute exposure of multiple species of animals to hydrazine by several routes of administration caused loss of appetite and weight, lethargy, vomiting, significant irritation of eyes, skin, and mucous membranes, hemolysis, fatty degeneration and lipid deposition in the liver and kidneys, and central nervous system (CNS) effects manifested by convulsions and death. Subchronic or chronic exposure of mice and rats to hydrazine by several routes of administration produced cancers of the liver, lung, or lymph tissues.

2. *Effects on humans*: A worker exposed to hydrazine hydrate once a week for six months developed fluid in the chest cavity, pulmonary edema, bronchitis, enlarged liver and kidneys, tissue destruction (necrosis) of the liver, intestinal hemorrhage, and death.

• Signs and symptoms of exposure

1. *Short-term (acute)*: Exposure to hydrazine can cause dizziness, nausea, skin burns, and irritation of the eyes, nose, and throat.

2. *Long-term (chronic)*: Exposure to hydrazine can cause lethargy, vomiting, tremors, itching and burning of the eyes and skin, conjunctivitis, and contact dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease.

The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to hydrazine, the 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, liver, kidneys, and hematopoietic (blood-cell forming), nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to hydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to hydrazine.

- **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to hydrazine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and hematopoietic, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

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

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

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of hydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting hydrazine vapors with hydrochloric acid-filled midjet bubblers and analyzing by visible absorption spectrophotometry. Direct-reading devices calibrated to measure hydrazine may also be used if available. A detailed sampling and analytical method for hydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 3503).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the

manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with hydrazine.

SANITATION

Clothing which is contaminated with hydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of hydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with hydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle hydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to hydrazine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for hydrazine

Operations	Controls
During use in the synthesis and handling of high-energy fuels, agricultural chemicals, pharmaceuticals, chemicals for plastics and rubber manufacturing, textile agents and dye intermediates, and photographic chemicals	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an anticorrosion agent; during use in the application of metal coatings on nonconducting materials	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to hydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to hydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hydrazine gets on the skin, wash it immediately with soap and water. If hydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If hydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing hydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing hydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Hydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should

not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for hydrazine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR HYDROQUINONE

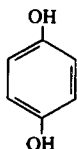
INTRODUCTION

This guideline summarizes pertinent information about hydroquinone for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₆H₆O₂

• **Structure:**



• **Synonyms:** 1,4-Benzenediol; dihydroxybenzene; hydroquinol; quinol

• **Identifiers:** CAS 123-31-9; RTECS MX3500000; DOT 2662

• **Appearance and odor:** Colorless to white crystalline solid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 110.11
2. Boiling point (at 760 mmHg): 285 °C (545 °F)
3. Specific gravity (water = 1): 1.332
4. Vapor density (air = 1 at boiling point of hydroquinone): 3.81
5. Melting point: 173 °C (344 °F)
6. Vapor pressure at 25 °C (77 °F): 1.8 x 10⁻⁵ mmHg
7. Solubility in water, g/100 g water at 25 °C (77 °F): 7
8. Evaporation rate (butyl acetate = 1): 1.8 x 10⁻⁶

• Reactivity

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving hydroquinone.
3. Caution: Airborne hydroquinone may be oxidized to quinone (C₆H₄O₂) at ordinary room temperatures in the presence of moisture.

• Flammability

1. Flash point: 165 °C (329 °F) (closed cup)
2. Autoignition temperature: 516 °C (960 °F)
3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
4. Combustible solid, Flammability Rating 1 (NFPA)

• Warning properties

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, hydroquinone should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hydroquinone is 2 milligrams of hydroquinone per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 2 mg/m³ [0.44 parts of hydroquinone per million parts of air (ppm)] as a ceiling concentration determined in any 15-minute sampling period. In those situations in which workers may be exposed to hydroquinone as a component of other materials at a concentration of 5% or less by weight, it should not be necessary to comply with the provisions of the standard; however, protection of workers' health should be insured by avoiding excessive contact with the chemical and by following effective cleaning procedures. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 2 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek.

**Table 1.—Occupational exposure limits
for hydroquinone**

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	—	2
NIOSH REL ceiling (15 min)	0.44	2
ACGIH TLV [®] TWA	—	2

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Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• Routes of exposure

Hydroquinone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute subcutaneous injection or oral administration of hydroquinone to multiple species of animals produced hypersensitivity to external stimuli, hyperactive reflexes, breathing difficulty (dyspnea), and bluish discoloration of skin and mucous membranes (due to methemoglobinemia), followed by convulsions, reduced body temperature, paralysis, loss of reflexes, coma, and death (due to decreased oxygen in the blood and respiratory failure). Subchronic or chronic exposure of multiple species of animals by the same routes of administration produced jaundice, anemia, hypoglycemia, increased white blood cell counts, increased cell fragility, depigmentation of skin or fur, and marked weight loss. Subchronic subcutaneous injection of hydroquinone into male rats caused reduction in the weights of sexual organs, sperm production, and fertility (as determined by reduced pregnancies). In mutagenicity tests, hydroquinone damaged DNA and chromosomes in bacteria.

2. *Effects on humans:* Chronic exposure of the eyes to hydroquinone has caused ulceration, opacity, and structural changes.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to hydroquinone can cause headache, dizziness, nausea, vomiting, increased respiration, breathing difficulty, sensation of suffocation, ringing noise in ears, paleness, bluish discoloration of skin, green or brownish-green discoloration of urine, and irritation of the skin and eyes.

2. *Long-term (chronic):* Exposure to hydroquinone can cause depigmentation of the skin, brownish discoloration of the cornea, and blurred vision.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of bio-

logic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to hydroquinone, the 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, gastrointestinal tract, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to hydroquinone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin and respiratory system.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to hydroquinone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, gastrointestinal tract, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations

of hydroquinone. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

Sampling and analysis may be performed by collecting hydroquinone with cellulose ester membrane filters followed by treatment with aqueous acetic acid and analysis by high-pressure liquid chromatography. A detailed sampling and analytical method for hydroquinone may be found in the *NIOSH Manual of Analytical Methods* (method number 5004).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum) and other appropriate protective clothing necessary to prevent skin contact with hydroquinone.

Workers should be provided with and required to use dust- and splash-proof safety goggles where hydroquinone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with hydroquinone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydroquinone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hydroquinone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with hydroquinone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle hydroquinone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to hydroquinone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for hydroquinone

Operations	Controls
During the preparation and use of photographic developers; during use in the dyeing and fur processing industries	Personal protective equipment
During use as an antioxidant; during use as a chemical stabilizer	Local exhaust ventilation, personal protective equipment
During the synthesis of hydroquinone ethers, vitamin E, hydroquinone diacetate, or p-methoxyphenol; during the synthesis and handling of hydroquinone powders	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to hydroquinone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hydroquinone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to hydroquinone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hydroquinone gets on the skin, wash it immediately with soap and water. If hydroquinone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If hydroquinone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Hydroquinone solid may be collected and placed in an appropriate container.
4. Hydroquinone solid or liquid may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.
5. For small quantities of liquids containing hydroquinone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from hydroquinone vapors. Burn the paper in a suitable location away from combustible materials.
6. Large quantities of liquids containing hydroquinone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Hydroquinone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for hydroquinone

Condition	Minimum respiratory protection*†
Concentration: Less than or equal to 50 mg/m ³	Any powered air-purifying respirator with a dust filter (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 100 mg/m ³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance causes eye irritation or damage—eye protection needed) Any supplied air respirator with tight-fitting facepiece operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 200 mg/m ³	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 200 mg/m ³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.44 ppm (2 mg/m³) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR INORGANIC ARSENIC AND ITS COMPOUNDS (as As) POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

"Inorganic arsenic" is defined as elemental arsenic and all of its inorganic compounds except arsine (see guideline for arsine). This guideline summarizes pertinent information about inorganic arsenic for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for elemental arsenic.

- **Formula:** As
- **Synonyms:** Arsenic black, arsenic-75, arsenic solid, arsenic metallic, arsenicals, grey arsenic
- **Identifiers:** CAS 7440-38-2; RTECS CG0525000; DOT 1558, label required: "Poison"
- **Appearance and odor:** Gray metal with an odor like garlic when heated

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for elemental arsenic.

- **Physical data**
 1. Molecular weight: 74.92
 2. Boiling point (at 760 mmHg): 613°C (1,135°F), sublimes
 3. Specific gravity (water = 1): 5.73
 4. Vapor density (air = 1 at sublimation point of arsenic): 2.6
 5. Melting point: Sublimes at 613°C (1,135°F)
 6. Insoluble in water
- **Reactivity**
 1. Incompatibilities: Oxidizing agents and heat
 2. Hazardous decomposition products: Toxic gases and vapors

or fumes (e.g., arsenic oxide fume) may be released in a fire involving arsenic.

3. Caution: Hydrogen gas can react with inorganic arsenic to form arsine.

- **Flammability**

1. Extinguishant: All firefighting agents, except soda-acid
2. Caution: Arsenic is combustible in powder form or by chemical reaction with powerful oxidizers such as bromates, chlorates, iodates, and peroxides.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for inorganic arsenic (except arsine) is 0.01 milligrams of arsenic per cubic meter of air (mg/m³) as a time-weighted average (TWA) over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that arsenic and all its inorganic compounds be controlled and handled as potential human carcinogens in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) for arsenic and all its inorganic compounds is 0.002 mg/m³ as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) for soluble arsenic compounds is 0.2 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek. The ACGIH has designated arsenic trioxide production as A2 (suspected human carcinogen) without having sufficient evidence to assign a TLV[®] (Table 1).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Inorganic arsenic compounds may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for inorganic arsenic and its compounds (as As)

	Arsenic and its inorganic compounds	Arsenic compounds, soluble	Arsenic trioxide production
	mg/m ³	mg/m ³	mg/m ³
OSHA PEL TWA	0.01	—	—
NIOSH REL (Ca)* Ceiling (15 min)	0.002	—	—
ACGIH TLV [®] (TWA)	—	0.2	(A2)†

* (Ca): NIOSH recommends treating as a potential human carcinogen.

† (A2): Suspected human carcinogen.

• Summary of toxicology

1. *Effects on animals:* Chronic ingestion or inhalation of inorganic arsenic by rats caused marked enlargement of the common bile duct and fatty degeneration of the liver. Injection of arsenic in pregnant rats, mice, and hamsters caused malformations of the offspring.

2. *Effects on humans:* Inhalation, ingestion, or dermal exposure of workers to inorganic arsenic has caused peripheral nerve inflammation (neuritis) and degeneration (neuropathy), reduced peripheral circulation, anemia, increased mortality due to cardiovascular failure, and cancers of the skin, lungs, and lymphatic system.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to inorganic arsenic can cause nausea, vomiting, diarrhea, weakness, loss of appetite, cough, chest pain, giddiness, headache, and breathing difficulty (dyspnea).

2. *Long-term (chronic):* Exposure to inorganic arsenic can cause weakness, nausea, vomiting, diarrhea, skin and eye irritation, hyperpigmentation, thickening of the palms and soles (hyperkeratosis), contact dermatitis, skin sensitization, warts, ulceration and perforation of the nasal septum, and numbness and weakness in the legs and feet.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and per-

sonal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to inorganic arsenic, the 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 skin, peripheral nervous system, liver, lymphatic and hematopoietic (blood cell forming) systems, and respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to inorganic arsenic and its compounds at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or peripheral neuropathy, a history and other findings consistent with chronic disease of the skin or nervous system, and significant breathing impairment due to preexisting chronic lung disease.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to inorganic arsenic. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, blood, lymphatic system, peripheral nervous system, liver, and respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH

and ATS: standardized questionnaires and tests of lung function.

- **Medical practices 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 which 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 to those expected for a suitable reference population. Because occupational exposure to inorganic arsenic and its compounds may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include: Inflammatory and toxic neuropathy, agranulocytosis or neutropenia (absence or a severe decrease in the number of certain white blood cells), and cancers of the liver and respiratory tract.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of inorganic arsenic. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting particulate inorganic arsenic with cellulose membrane filters followed by digestion with acid and analysis by atomic absorption with flame arsine generation. A detailed sampling and analytical method may be found in the *NIOSH Manual of Analytical Methods* (method number 7900).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with inorganic arsenic.

SANITATION

Clothing which is contaminated with inorganic arsenic should be removed immediately and placed in sealed containers for

storage until it can be discarded or until provision is made for the removal of inorganic arsenic from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of inorganic arsenic's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with inorganic arsenic should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle inorganic arsenic should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to inorganic arsenic may occur and control methods which may be effective in each case are listed in Table 2.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to inorganic arsenic, an eyewash fountain should be provided within the immediate work area for emergency use.

If inorganic arsenic gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to inorganic arsenic, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If inorganic arsenic gets on the skin, wash it immediately with soap and water. If inorganic arsenic penetrates the clothing, remove the clothing promptly and wash the skin with soap and water. Get medical attention promptly.

Table 2.—Operations and methods of control for inorganic arsenic

Operations	Controls
During the manufacture of insecticides, weed killers and fungicides; during use as a wood preservative	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the manufacture and handling of calcium arsenate; during use in the manufacture of electrical semiconductors, diodes, and solar batteries	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a bronzing or decolorizing addition in glass manufacturing; during use in the production of opal glass and enamels	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an addition to alloys to increase hardening and heat resistance	Process enclosure, local exhaust ventilation, personal protective equipment
During smelting of ores	Local exhaust ventilation, personal protective equipment

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If inorganic arsenic or its compounds are spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities of liquids containing inorganic arsenic, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing inorganic arsenic may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Inorganic arsenic dust may be collected by vacuuming with an appropriate high-efficiency filtration system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for inorganic arsenic

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted acid gas canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR INORGANIC LEAD

INTRODUCTION

"Inorganic lead" is defined as lead oxides, metallic lead, and lead salts (including organic salts such as lead soaps but excluding lead arsenate). This guideline summarizes pertinent information about inorganic lead for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** Pb
- **Synonyms:** C.I. pigment metal 4, C.I. 77575, KS-4, lead flake, lead S2
- **Identifiers:** CAS 7439-92-1; RTECS OF7525000; DOT 1794
- **Appearance and odor:** Bluish-white, silvery, or gray odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 207.19
 2. Boiling point (at 760 mmHg): 1,740°C (3,164°F)
 3. Specific gravity (water = 1): 11.34
 4. Melting point: 327.5°C (621.5°F)
 5. Insoluble in water
- **Reactivity**
 1. Incompatibilities: Lead reacts vigorously with oxidizing materials. Contact with hydrogen peroxide or active metals such as sodium or potassium may cause fires or explosions.
 2. Hazardous decomposition products: Toxic fumes (e.g., lead oxide) may be released in a fire involving inorganic lead.
- **Flammability**
 1. Extinguishant: Dry sand, dry dolomite, or dry graphite
 2. Caution: Lead is combustible in powder form when exposed to heat or flame

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, inorganic lead should be treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for inorganic lead is 50 micrograms of lead per cubic meter of air ($\mu\text{g}/\text{m}^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift. If a worker is exposed to lead for more than 8 hours in any workday, the PEL, as a TWA for that day, shall be reduced according to the following formula: maximum permissible limit (in $\mu\text{g}/\text{m}^3$) = 400 divided by hours worked in the day. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 100 $\mu\text{g}/\text{m}^3$ as a TWA for up to a 10-hour workshift, 40-hr. workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 0.15 mg/m^3 (150 $\mu\text{g}/\text{m}^3$) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

**Table 1.—Occupational exposure limits
for inorganic lead**

	Exposure units $\mu\text{g}/\text{m}^3$
OSHA PEL TWA	50
NIOSH REL TWA	100*
ACGIH TLV [®] TWA	150

* Air level to be maintained such that worker blood lead remains $\leq 60 \mu\text{g}/100\text{g}$.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Inorganic lead may cause adverse health effects following exposure via inhalation or ingestion.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Summary of toxicology**

1. *Effects on animals*: In rats or mice, chronic oral administration or subcutaneous or intraperitoneal injection of lead subacetate, lead acetate, or lead phosphate produced cancer of the kidneys. Intravenous or intraperitoneal injection of lead nitrate, lead acetate, or lead chloride to pregnant mice, rats, or hamsters caused increased fetal mortality and malformations of the posterior extremities and urogenital and intestinal tracts in the offspring.

2. *Effects on humans*: Inhalation or ingestion of inorganic lead has caused peripheral neuropathy with paralysis of the muscles of the wrists and ankles, encephalopathy, anemia (due to decreased red blood cell life and impaired heme synthesis), proximal kidney tubule damage, decreased kidney function, and chronic kidney disease. Lead can accumulate in the soft tissues and bones, with the highest accumulation in the liver and kidneys, and elimination is slow. Lead can penetrate the placental barrier, resulting in neurologic disorders in infants.

- **Signs and symptoms of exposure**

1. *Short-term (acute)*: Exposure to inorganic lead can cause decreased appetite, insomnia, headache, muscle and joint pain, colic, and constipation.

2. *Long-term (chronic)*: Exposure to inorganic lead can cause weakness, weight loss, nausea, vomiting, constipation, blue or blue-black dot-like pigmentation on the gums ("lead line"), severe headache and abdominal cramps, delirium, convulsions, and coma.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to inorganic lead, the 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 kidneys and the hematopoietic (blood cell forming), nervous, gastrointestinal, and reproductive systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to inorganic lead at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include preexisting neuromuscular disease. In addition to the medical interview and physical examination, the physician should consider obtaining additional baseline electrophysiologic and electromyographic studies and an assessment of fertility, using standardized methods and evaluation criteria. The physician should also obtain baseline values for the complete blood count including the reticulocyte count and for those tests which characterize prior internal exposure (e.g., blood lead level) and the effects of prior exposures (e.g., erythrocyte zinc protoporphyrin and delta-aminolevulinic acid dehydrogenase).

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to inorganic lead. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the kidneys and the hematopoietic (blood cell forming), nervous, gastrointestinal, and reproductive systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria: a complete blood count with reticulocyte count and those tests which characterize prior internal exposure (e.g., blood lead level) and the effects of exposures (e.g., erythrocyte zinc protoporphyrin and delta-aminolevulinic acid dehydrogenase).

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to inorganic lead may cause adverse reproductive effects and diseases of prolonged induction-

latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Acute renal failure.
2. Delayed-onset or reproductive SHE's include: Inflammatory and toxic neuropathy and chronic renal failure.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to inorganic lead should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting inorganic lead with cellulose membrane filters followed by acid digestion and analysis by atomic absorption. A detailed sampling and analytical method for inorganic lead may be found in the *NIOSH Manual of Analytical Methods* (method number 7082).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum) and other appropriate protective clothing necessary to prevent skin contact with inorganic lead.

Workers should be provided with and required to use dust-proof safety goggles where inorganic lead may come in contact with the eyes.

SANITATION

Clothing which is contaminated with inorganic lead should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of inorganic lead from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of inorganic lead's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with inorganic lead should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the

storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle inorganic lead should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to inorganic lead may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for inorganic lead

Operations	Controls
During primary (ore) and secondary (scrap) smelting of lead; during the manufacture of storage batteries; during typecasting and remelting of type metal in printing	Process enclosure, local exhaust ventilation, dust control, personal protective equipment
During soldering in the fabrication of metal articles	Process enclosure, local exhaust ventilation, personal protective equipment
During melting and pouring of lead and alloys containing lead; during welding, burning, and cutting of metal structures containing lead or painted with lead containing surface coatings	Local exhaust ventilation, personal protective equipment
During the use of lead in the manufacture of surface coatings, including paints and varnishes; during the manufacture of ceramics and glass	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to inorganic lead, an eye-wash fountain should be provided within the immediate work area for emergency use.

If inorganic lead gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this compound.

• Skin exposure

Where there is any possibility of a worker's body being exposed to inorganic lead, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If inorganic lead gets on the skin, wash it immediately with soap and water. If inorganic lead penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If inorganic lead is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing inorganic lead, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing inorganic lead may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. If in solid form, inorganic lead may be collected and placed in an appropriate container.
6. Inorganic lead may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection

program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for inorganic lead

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.5 mg/m ³	Any supplied air respirator Any air-purifying respirator with a high-efficiency particulate filter Any self-contained breathing apparatus
Less than or equal to 1.25 mg/m ³	Any powered air-purifying respirator with a high-efficiency particulate filter Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 2.5 mg/m ³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 50 mg/m ³	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Less than or equal to 100 mg/m ³	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 100 mg/m ³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 100 µg/m³ (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR METHYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about methyl mercaptan for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** CH₄S
- **Structure:** CH₃-SH
- **Synonyms:** Mercaptomethane, methanethiol, methyl sulfhydrate, thiomethyl alcohol
- **Identifiers:** CAS 74-93-1; RTECS PB4375000; DOT 1064, label required: "Flammable Gas"
- **Appearance and odor:** Colorless gas with an odor like decaying cabbage

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 48.11
 2. Boiling point (at 760 mmHg): 5.96°C (40.4°F)
 3. Specific gravity (water = 1): 0.8665
 4. Vapor density (air = 1 at boiling point of methyl mercaptan): 1.66
 5. Melting point: -123°C (-190°F)
 6. Vapor pressure at 20°C (68°F): 1,276 mmHg
 7. Solubility in water, g/100 g water at 20°C (68°F): 2.4
 8. Ionization potential: 9.44 eV
- **Reactivity**
 1. Incompatibilities: Strong oxidizing agents. Elevated temperature may generate high internal pressure and cause containers to burst.
 2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving methyl mercaptan.

3. Caution: Liquid methyl mercaptan will attack some forms of plastics, coatings, and rubber.

• Flammability

1. Flash point: -18°C (0°F) (open cup)
2. Flammable limits in air, % by volume: Lower, 3.9; upper, 21.8
3. Extinguishant: Carbon dioxide, dry chemicals, or alcohol foam
4. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)

• Warning properties

1. Odor threshold: 1 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, methyl mercaptan can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for methyl mercaptan is 10 parts of methyl mercaptan per million parts of air (ppm) [20 milligrams of methyl mercaptan per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.5 ppm (1.0 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 0.5 ppm (1 mg/m³) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for methyl mercaptan

	Exposure limits	
	ppm	mg/m ³
OSHA PEL ceiling	10	20
NIOSH REL ceiling (15 min)	0.5	1.0
ACGIH TLV [®] TWA	0.5	1.0

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HEALTH HAZARD INFORMATION

• Routes of exposure

Methyl mercaptan may cause adverse health effects following exposure via inhalation or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of methyl mercaptan by rats and mice caused restlessness, increased respiration, muscular weakness progressing to paralysis, convulsions, respiratory depression, deficient oxygenation of the blood (cyanosis), and death due to respiratory paralysis. Subchronic inhalation of methyl mercaptan by monkeys, rats, and mice caused altered blood chemistries in all three species, pulmonary edema in monkeys, and persistent hepatitis and cellular changes of the liver, lungs, and kidneys in mice.

2. *Effects on humans:* An accidental industrial exposure of a worker to methyl mercaptan caused elevated blood pressure, severe hemolytic anemia, methemoglobinemia, deep coma, and death due to pulmonary embolus 28 days following exposure.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to methyl mercaptan can cause headache, dizziness, staggered gait, nausea, vomiting, pulmonary irritation, expiratory wheezing, rapid heart beat (tachycardia), rigidity of the arms and legs, bluish discoloration of the skin and mucous membranes (cyanosis), and irritation of the eyes and mucous membranes.

2. *Long-term (chronic):* Low-level exposure to methyl mercaptan can cause dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, in-

cluding employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to methyl mercaptan, the 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 skin and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to methyl mercaptan at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin and respiratory system.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to methyl mercaptan. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of methyl mercaptan. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker)

should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

There are no NIOSH-validated sampling and analytical methods for methyl mercaptan. Direct reading devices calibrated to measure methyl mercaptan may be used if available.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with methyl mercaptan.

Workers should be provided with and required to use splash-proof safety goggles where liquid methyl mercaptan may come in contact with the eyes.

SANITATION

Clothing which is contaminated with liquid methyl mercaptan should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl mercaptan from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of methyl mercaptan's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with methyl mercaptan should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle methyl mercaptan should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to methyl mercaptan may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for methyl mercaptan

Operations	Controls
During use in the manufacture and processing of methyl mercaptan and methionine; during use as a catalyst or activator; during use in wood processing	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in the synthesis of chemical intermediates for the manufacture of resins, plastics, insecticides, and pressure-sensitive and oil-resistant adhesives	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as an odorant and warning agent in natural gas; during use in jet fuels; during the cleaning and maintenance of storage containers	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to methyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If methyl mercaptan gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to methyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If methyl mercaptan gets on the skin, wash it immediately with soap and water. If methyl mercaptan penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If methyl mercaptan is spilled or leaked, the following steps should be taken:

1. If methyl mercaptan is in the gaseous form, stop the flow of gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air and repair the leak or allow the cylinder to empty.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing methyl mercaptan, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood duct work is free from methyl mercaptan vapors. Burn the paper in a suitable location away from combustible material.
5. Large quantities of liquids containing methyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Methyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
6. Liquids containing methyl mercaptan may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic en-

vironmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for methyl mercaptan

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator Any self-contained breathing apparatus Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 12.5 ppm	Any supplied-air respirator operated in a continuous flow mode Any powered air-purifying respirator with organic vapor cartridge(s)
Less than or equal to 25 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 400 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 400 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 ppm (1.0 mg/m³) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR MONOMETHYL HYDRAZINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about monomethyl hydrazine for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** CH₆N₂
- **Structure:** CH₃NHNH₂
- **Synonyms:** Hydrazomethane, 1-methyl hydrazine, methyl hydrazine, MMH
- **Identifiers:** CAS 60-34-4; RTECS MV5600000; DOT 1244, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Colorless liquid with a strong ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 46.09
 2. Boiling point (at 760 mmHg): 87.5°C (189°F)
 3. Specific gravity (water = 1): 0.874
 4. Vapor density (air = 1 at boiling point of monomethyl hydrazine): 1.59
 5. Melting point: -52.4°C (-61.6°F)
 6. Vapor pressure: At 20°C (68°F): 36.0 mmHg; at 25°C (77°F), 49.6 mmHg
 7. Soluble in water
 8. Evaporation rate (butyl acetate = 1): 1.5
 9. Saturation concentration in air (approximate) at 25°C (77°F): 6.5% (65,300 ppm)
 10. Ionization potential: 7.67 eV
- **Reactivity**

Incompatibilities: Monomethyl hydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and

with manganese, lead, copper, or their alloys can lead to fires and explosions.

Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving monomethyl hydrazine.

Caution: Monomethyl hydrazine will attack cork, some forms of plastics, coatings, and rubber.

• Flammability

1. Flash point: -8.3°C (17°F) (closed cup)
2. Autoignition temperature: 194°C (382°F)
3. Flammable limits in air, % by volume: Lower, 2.5; upper, 92
4. Extinguishant: Alcohol foam, dry chemical, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Monomethyl hydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

• Warning properties

1. Odor threshold: 1-3 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for monomethyl hydrazine is 0.2 parts of monomethyl hydrazine per million parts of air (ppm) [0.35 milligrams of monomethyl hydrazine per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that monomethyl hydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is

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0.04 ppm (0.08 mg/m³) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated monomethyl hydrazine as an A2 substance (suspected human carcinogen) having an assigned threshold limit value ceiling (TLV[®]-C), the concentration that should not be exceeded during any part of the working exposure, of 0.2 ppm (0.35 mg/m³) (Skin) (Table 1).

Table 1.—Occupational exposure limits for monomethyl hydrazine

	Exposure limits	
	ppm	mg/m ³
OSHA PEL		
Ceiling (Skin)*	0.2	0.35
NIOSH REL (Ca)†		
Ceiling (120 min)	0.04	0.08
ACGIH TLV [®] (A2)‡		
Ceiling (Skin)	0.2	0.35

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

‡ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Monomethyl hydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

Effects on animals: Acute inhalation of monomethyl hydrazine by dogs caused respiratory irritation, pulmonary hemorrhage and edema, central nervous system stimulation, and convulsions; acute subcutaneous injection in dogs caused damage to the kidneys (including hemoglobinuria, hyaline droplet degeneration, and severe renal epithelial damage). Subchronic inhalation of monomethyl hydrazine by dogs, monkeys, rats, or mice produced nose and eye irritation, diarrhea, rapid respiration, deficient oxygenation of the blood (cyanosis), impaired muscular coordination (ataxia), tremors, convulsions, blood disorders (including significant hemolysis and hemolytic anemia), increased storage of iron in the body (hemosiderosis), and reduced bile flow (cholestasis). Chronic oral administration of monomethyl hydrazine to mice produced lung tumors; hamsters similarly exposed developed liver cancer.

• Signs and symptoms of exposure

Short-term (acute): Monomethyl hydrazine can cause irritation of the eyes and respiratory tract, nausea, diarrhea, and convulsions.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance

intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to monomethyl hydrazine, the 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, liver, kidneys, and hematopoietic (blood-cell-forming), respiratory, and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to monomethyl hydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver, kidneys, and hematopoietic and respiratory systems. The physician should obtain baseline values for liver function tests. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to monomethyl hydrazine.

- **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to monomethyl hydrazine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, liver, kidneys, and hematopoietic, respiratory, and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and lung function tests.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to monomethyl hydrazine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of monomethyl hydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting monomethyl hydrazine vapors with sulfuric-acid-coated silica gel tubes and analyzing by gas chromatography. Direct-reading devices calibrated to measure monomethyl hydrazine may also be used if available. A detailed sampling and analytical method for monomethyl hydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the

manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with monomethyl hydrazine.

SANITATION

Clothing which is contaminated with monomethyl hydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of monomethyl hydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of monomethyl hydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with monomethyl hydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle monomethyl hydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to monomethyl hydrazine may occur and control methods which may be effective in each case are listed in Table 2.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to monomethyl hydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If monomethyl hydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

Table 2.—Operations and methods of control for monomethyl hydrazine

Operations	Controls
During use in the preparation and handling of liquid rocket propellants; during use as a chemical intermediate for the synthesis of pesticides	Process enclosure, local exhaust ventilation, personal protective equipment
During use in polymer technology and in miscellaneous processes such as electroplating, etching, and photographic processing	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture and distribution of monomethyl hydrazine; during maintenance of storage containers	Process enclosure, local exhaust ventilation, personal protective equipment

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to monomethyl hydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If monomethyl hydrazine gets on the skin, wash it immediately with soap and water. If monomethyl hydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If monomethyl hydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing monomethyl hydrazine may be flushed with water; the waste water may then be collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing monomethyl hydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Monomethyl hydrazine should not be

allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for monomethyl hydrazine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR NITROGLYCERIN AND ETHYLENE GLYCOL DINITRATE

INTRODUCTION

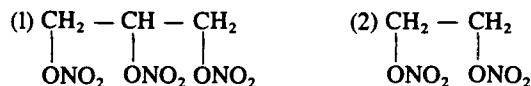
This guideline summarizes pertinent information about nitroglycerin (NG) and ethylene glycol dinitrate (EGDN) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate.

• **Formula:** (1) $C_3H_5N_3O_9$ (2) $C_2H_4N_2O_6$

• **Structure:**



• **Synonyms:** (1) Anginine, blasting gelatin, blasting oil, glonoin, glycerol trinitrate, glyceryl nitrate, glyceryl trinitrate, GTN, myocon, NG, niglycon, niong, nitric acid triester of glycerol, nitrine-TDC, nitroglycerol, nitroglycn, nitrol; (2) Dinitroglycol, EGDN, ethanediol dinitrate, ethylene dinitrate, ethylene nitrate, glycol dinitrate, nitroglycol

• **Identifiers:** (1) CAS 55-63-0; RTECS QX2100000; DOT not assigned; (2) CAS 628-96-6; RTECS KW5600000; DOT not assigned

• **Appearance and odor:** (1) Pale yellow, slightly sweet smelling oil; (2) yellowish liquid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate. If not specified, data apply to both compounds.

• **Physical data**

1. Molecular weight: (1) 227.11; (2) 152.08
2. Boiling point (at 760 mmHg): (1) 256°C (493°F); (2) 197-200°C (387-392°F)

3. Explosive point: (1) 270°C (518°F); (2) 114°C (237°F)
4. Specific gravity (water = 1): (1) 1.6; (2) 1.49
5. Vapor density: (1) 7.8 (air = 1 at boiling point of NG); (2) 5.24 (air = 1 at boiling point of EGDN)
6. Melting point: (1) 13.1°C (55.1°F); (2) -22.3°C (-9°F)
7. Vapor pressure at 20°C (68°F): (1) 0.00012-0.011 mmHg; (2) 0.04 mmHg
8. (1) Slightly soluble in water; (2) insoluble in water

• Reactivity

1. Incompatibilities: Contact with acids, heat, or mechanical shock may result in explosion.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in an explosion involving NG or EGDN.

• Flammability

1. Flash point: Explodes

2. Autoignition temperature: (1) 270.4°C (518°F); (2) 195°C (383°F)

3. Class A Explosive (29 CFR 1910.109), Flammability Rating 2 (NFPA)

• Warning properties

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, NG and EGDN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for NG and EGDN is 0.2 parts of NG or EGDN per million parts of air (ppm) [2 milligrams of NG or 1 milligram of EGDN per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for NG or EGDN alone or for mixtures of the two substances is 0.1 mg/m³ as a ceiling concentration determined in any 20-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for NG or EGDN is

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

0.05 ppm (0.5 mg/m³ NG or 0.3 mg/m³ EGDN) as a time-weighted average concentration (TWA) for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational exposure limits for nitroglycerin and ethylene glycol dinitrate

	Exposure limits	
	ppm	mg/m ³
OSHA PEL		
NG ceiling (Skin)*	0.2	2
EGDN ceiling (Skin)†	0.2	1
NIOSH REL		
Ceiling (20 min)	—	0.1
ACGIH TLV®		
NG TWA (Skin)	0.05	0.5
EGDN TWA (Skin)	0.05	0.3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† If the atmospheric concentration of EGDN exceeds 0.02 ppm, personal protection may be necessary to avoid headache.

HEALTH HAZARD INFORMATION

• Routes of exposure

NG and EGDN may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• Summary of toxicology

1. *Effects on animals*: Subchronic inhalation of EGDN by mice caused lethargy, skin damage, muscle spasms, and death due to circulatory and respiratory paralysis. In cats, subchronic or chronic inhalation or dermal administration of EGDN caused severe anemia, decreased appetite, seizures, hemorrhage of internal organs, and death. Chronic oral administration of NG to rats produced cancer of the liver. NIOSH will continue to monitor the research regarding NG to determine whether the collective evidence justifies controlling this chemical as a carcinogen.

2. *Effects on humans*: Acute inhalation or dermal exposure of workers to NG and EGDN has caused decreased systolic, diastolic, and pulse blood pressures due to vascular dilation. Chronic exposure to NG and EGDN has caused damage to the heart and reduced tolerance to alcohol. Chronic exposure to NG and EGDN, or to NG alone, followed by a brief or extended period away from exposure, has been associated with an increased incidence of sudden death.

• Signs and symptoms of exposure

1. *Short-term (acute)*: Exposure to NG and EGDN can cause severe headache, dizziness, nausea, and heart palpitations.

2. *Long-term (chronic)*: Exposure to NG and EGDN can cause severe chest pain (angina pectoris), which frequently occurs during brief periods away from work. Skin sensitization can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance

intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to NG or EGDN, the 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 skin and nervous, cardiovascular, and hematopoietic (blood-cell-forming) systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to NG or EGDN at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history and physical or other findings suggestive of cardiovascular disease, especially coronary artery disease. The physician should obtain baseline values for electrocardiographic studies appropriate for the age and medical history of the worker.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to NG or EGDN. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and nervous, hematopoietic, and cardiovascular sys-

tems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to NG or EGDN may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include methemoglobinemia.
2. Delayed-onset SHE's include methemoglobinemia and chest pain (angina pectoris).

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of NG and EGDN. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 20-minute sample or a series of consecutive samples that total 20 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

Sampling and analysis may be performed by collecting NG and EGDN vapors with tenax solid sorbent tubes followed by desorption with ethanol and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure NG and EGDN may also be used if available. A detailed sampling and analytical method for NG and EGDN may be found in the *NIOSH Manual of Analytical Methods* (method number 2507).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with NG and EGDN.

Workers should be provided with and required to use splash-proof safety goggles where NG or EGDN may come in contact with the eyes.

SANITATION

Clothing which is contaminated with NG or EGDN should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of NG and EGDN from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of NG and EGDN's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with NG or EGDN should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle NG or EGDN should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to NG and EGDN may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for nitroglycerin and ethylene glycol dinitrate

Operations	Controls
During formulation and filling operations in the manufacture of industrial explosives and propellants	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the synthesis and handling of NG or EGDN; during the handling of industrial explosives	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the preparation and handling of dosage forms including tablets and solutions in the manufacture of pharmaceuticals	Process enclosure, local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to NG or EGDN, an eye-wash fountain should be provided within the immediate work area for emergency use.

If NG or EGDN gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with these compounds.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to NG or EGDN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If NG or EGDN gets on the skin, wash it immediately with soap and water. If NG or EGDN penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If NG or EGDN is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing NG or EGDN, absorb on sponges or paper towels kept in a sodium carbonate solution. Remove paper towels to a secure outdoor location for burning.
4. Large quantities of liquids containing NG or EGDN may be washed with water into holding tanks where NG and EGDN can be separated. NG and EGDN should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in solid form, NG and EGDN may be collected using non-sparking tools and removed to a secure, outdoor location for burning.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should

not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for nitroglycerin and ethylene glycol dinitrate

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.2 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 0.5 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 2 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 20 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 40 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 40 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.1 mg/m³ (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR N-NITROSODIMETHYLAMINE POTENTIAL HUMAN CARCINOGEN

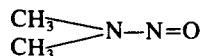
INTRODUCTION

This guideline summarizes pertinent information about N-nitrosodimethylamine for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₂H₆N₂O

• **Structure:**



• **Synonyms:** Dimethylnitrosamine; N,N-dimethylnitrosamine; dimethylnitrosoamine; DMN; DMNA; N-methyl-N-nitrosomethanamine; NDMA; nitrosodimethylamine

• **Identifiers:** CAS 62-75-9; RTECS IQ0525000; DOT not assigned

• **Appearance and odor:** Yellow liquid of low viscosity

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 74.10
2. Boiling point (at 760 mmHg): 152°C (305.6°F)
3. Specific gravity (water = 1): 1.005
4. Vapor density (air = 1 at boiling point of N-nitrosodimethylamine): 2.56
5. Soluble in water

• **Reactivity**

1. Incompatibilities: Ultraviolet light; strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving N-nitrosodimethylamine.
3. Caution: Store in dark bottles.

• **Flammability**

Extinguishant: Dry chemical, alcohol foam, or carbon dioxide

• **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for N-nitrosodimethylamine; however, the OSHA standard requires implementation of stringent controls wherever N-nitrosodimethylamine or solid or liquid mixtures containing at least 0.1% by weight or volume of N-nitrosodimethylamine are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1016, N-Nitrosodimethylamine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated N-nitrosodimethylamine as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

N-nitrosodimethylamine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• **Summary of toxicology**

1. *Effects on animals:* Acute intraperitoneal injection of N-nitrosodimethylamine in rats produced cancer of the nasal cavity. In multiple species of animals, subchronic or chronic exposure via several routes of administration produced cancers of the liver, kidneys, or lungs. Intravenous or interplacental injections of N-nitrosodimethylamine in rats caused increased embryoletality and fetal mortality.

2. *Effects on humans:* Acute exposure of laboratory workers to N-nitrosodimethylamine has caused inflammation, degeneration, cirrhosis, and dysfunction of the liver and death.

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- **Signs and symptoms of exposure**

Short-term (acute): Exposure to N-nitrosodimethylamine can cause vomiting, abdominal cramps, diarrhea, headache, fever, and jaundice.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to N-nitrosodimethylamine, the 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 liver, kidneys, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to N-nitrosodimethylamine. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to N-nitrosodimethylamine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity of and physiologic function of the liver, kidneys, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to N-nitrosodimethylamine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting N-nitrosodimethylamine vapors with Tenax GC in short glass tubes followed by desorption by heating and purging with helium, separation by capillary gas-liquid chromatography, and analysis by mass spectrometry. Direct-reading devices calibrated to measure N-nitrosodimethylamine may also be used if applicable. A detailed sampling and analytical method for N-nitrosodimethylamine may be found in the *NIOSH Manual of Analytical Methods* (method number 252).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where N-nitrosodimethylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place

used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where N-nitrosodimethylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with N-nitrosodimethylamine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of N-nitrosodimethylamine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of N-nitrosodimethylamine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove N-nitrosodimethylamine from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1016:

Areas where N-nitrosodimethylamine is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers are permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited

to the nature of the carcinogenic hazards of N-nitrosodimethylamine, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving N-nitrosodimethylamine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of N-nitrosodimethylamine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where N-nitrosodimethylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of N-nitrosodimethylamine shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove N-nitrosodimethylamine from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to N-nitrosodimethylamine may occur and control methods which may be effective in each case are listed in Table 1.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergen-

Table 1.—Operations and methods of control for N-nitrosodimethylamine

Operations	Controls
During use in the production of rocket fuel; during use as a solvent in the fibers and plastics industries, as an oxidant, and as an additive in lubricants	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substance

cy procedures. If a worker has contact with N-nitrosodimethylamine, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to N-nitrosodimethylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If N-nitrosodimethylamine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to N-nitrosodimethylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If N-nitrosodimethylamine gets on the skin, wash it immediately with soap and water. If N-nitrosodimethylamine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If N-nitrosodimethylamine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities liquids containing N-nitrosodimethylamine, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing N-nitrosodimethylamine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. Liquids containing N-nitrosodimethylamine may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for N-nitrosodimethylamine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-PENTANONE

INTRODUCTION

This guideline summarizes pertinent information about 2-pentanone for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₅H₁₀O

• **Structure:**

$$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$$

• **Synonyms:** Ethyl acetone, methyl n-propyl ketone, MPK

• **Identifiers:** CAS 107-87-9; RTECS SA7875000; DOT 1249, label required: "Flammable Liquid"

• **Appearance and odor:** Colorless liquid with a powerful, ethereal, fruity odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 86.15
2. Boiling point (at 760 mmHg): 102.3°C (216°F)
3. Specific gravity (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of 2-pentanone): 3.0
5. Melting point: -77.5°C (-108°F)
6. Vapor pressure at 25°C (77°F): 16 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 4.3
8. Evaporation rate (butyl acetate = 1): 1.25
9. Saturation concentration in air (approximate) at 25°C (77°F): 2.1% (21,000 ppm)
10. Ionization potential: 9.37 eV

• Reactivity

1. Incompatibilities: Oxidizing agents may cause fires and explosions

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving 2-pentanone
3. Caution: 2-Pentanone will dissolve some plastics, resins, and rubber.

• Flammability

1. Flash point: 7.2°C (45°F) (closed cup)
2. Autoignition temperature: 452°C (846°F)
3. Flammable limits in air, % by volume: Lower, 1.6; Upper, 8.2
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

• Warning properties

1. Odor threshold: 11 ppm
2. Eye irritation levels: Humans exposed to 2-pentanone at 1,300 to 1,500 ppm found brief exposure severely irritating to the eyes, but no damage was produced.
3. Evaluation of warning properties for respirator selection: Because of its odor, 2-pentanone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, 2-pentanone is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-pentanone is 200 parts of 2-pentanone per million parts of air (ppm) [700 milligrams per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 150 ppm (530 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 200 ppm (700 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 250 ppm (875 mg/m³) (Table 1).

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Table 1.—Occupational exposure limits for 2-pentanone

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	200	700
NIOSH REL TWA	150	530
ACGIH TLV® TWA	200	700
STEL	250	875

HEALTH HAZARD INFORMATION

• Routes of exposure

2-Pentanone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of 2-pentanone by guinea pigs caused narcosis and congestion, hemorrhage, and edema of the lungs, liver, and kidneys.

2. *Effects on humans:* Acute inhalation of 2-pentanone has caused narcosis and central nervous system depression.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to 2-pentanone can cause headache, nausea, dizziness, vomiting, incoordination, and irritation of the eyes and respiratory passages.

2. *Long-term (chronic):* Dermal exposure to liquid 2-pentanone can cause dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals,

potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to 2-pentanone, the 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, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-pentanone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-pentanone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices 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 which 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 to those expected for a suitable reference population.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to 2-pentanone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under cer-

tain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting 2-pentanone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure 2-pentanone may also be used if available. A detailed sampling and analytical method for 2-pentanone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with 2-pentanone.

Workers should be provided with and required to use splash-proof safety goggles where 2-pentanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with 2-pentanone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-pentanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-pentanone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with 2-pentanone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-pentanone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-pentanone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 2-pentanone

Operations	Controls
During application of cellulose- or resin-based coatings, finishes, and adhesives	Local exhaust ventilation, general dilution ventilation
During oven or air drying of coatings, finishes, and adhesives; during use in the manufacture of pharmaceuticals and some flavorings; during use as an extractant in dewaxing petroleum products	General dilution ventilation
During blending of raw materials for molded plastics	Local exhaust ventilation, personal protective equipment
During cleaning and maintenance of ketone-processing equipment	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 2-pentanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-pentanone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to 2-pentanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-pentanone gets on the skin, wash it immediately with soap and water. If 2-pentanone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 2-pentanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing 2-pentanone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from 2-pentanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing 2-pentanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. 2-Pentanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing 2-pentanone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforce-

ment and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors and meet other requirements of the decision logic may also be used.

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Table 3.—Respiratory protection for 2-pentanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection) Any powered air-purifying respirator with organic vapor cartridge(s)(substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1,500 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 3,750 ppm	Any supplied-air respirator operated in continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 5,000 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 5,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

*Only NIOSH/MSHA-equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 150 ppm (530 mg/m³ (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PHENYLHYDRAZINE POTENTIAL HUMAN CARCINOGEN

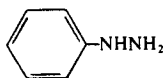
INTRODUCTION

This guideline summarizes pertinent information about phenylhydrazine for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₆H₈N₂

• **Structure:**



• **Synonyms:** Hydrazinobenzene, hydrazine-benzene

• **Identifiers:** CAS 100-63-0; RTECS MV8925000; DOT 2572, label required: "Poison"

• **Appearance and odor:** Pale yellow crystals or oily liquid with a faint aromatic odor; color darkens upon exposure to air and light

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 108.16
2. Boiling point (at 760 mmHg): 243.5 °C (471 °F) with decomposition
3. Specific gravity (water = 1): 1.0978
4. Vapor density (air = 1 at boiling point of phenylhydrazine): 3.7
5. Melting point: 19.6 °C (68 °F)
6. Vapor pressure at 25 °C (77 °F): 0.04 mmHg
7. Slightly soluble in water
8. Evaporation rate (butyl acetate = 1): 0.4
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 50 ppm
10. Ionization potential: 7.66 eV

• Reactivity

1. Incompatibilities: Phenylhydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and

with manganese, lead, copper, or their alloys can lead to fires and explosions.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving phenylhydrazine.

3. Caution: Phenylhydrazine will attack cork, some forms of plastics, coatings, and rubber.

• Flammability

1. Flash point: 88 °C (190 °F) (closed cup)
2. Autoignition temperature: 174 °C (345 °F)
3. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or large quantities of coarse water spray
4. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)
5. Caution: Phenylhydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth, or with oxidants such as hydrogen peroxide or nitric acid.

• Warning properties

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for phenylhydrazine is 5 parts of phenylhydrazine per million parts of air (ppm) [22 milligrams of phenylhydrazine per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that phenylhydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.14 ppm (0.6 mg/m³) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated phenylhydrazine as an A2 substance (suspected hu-

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

man carcinogen) having an assigned threshold limit value (TLV®) of 5 ppm (20 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short term exposure limit (STEL) is 10 ppm (45 mg/m³) (Table 1).

Table 1.— Occupational exposure limits for phenylhydrazine

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA (Skin)*	5	22
NIOSH REL (Ca)† ceiling (120 min)	0.14	0.6
ACGIH TLV® TWA (Skin) (A2)§	5	20
STEL (Skin) (A2)	10	45

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Phenylhydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute subcutaneous or intraperitoneal injection of phenylhydrazine hydrochloride in mice, rats, or dogs caused deficient oxygenation of the blood (cyanosis), breathing difficulty (dyspnea), convulsions, severe hemolytic anemia, or degenerative lesions of the liver and kidneys. Subchronic oral administration of phenylhydrazine to mice produced tumors of the blood vessels and cancer of the lungs. Phenylhydrazine injected into pregnant rats reduced certain learning abilities in the offspring by inducing severe neonatal jaundice and anemia.

2. *Effects on humans:* Exposure of workers to phenylhydrazine has caused hemolytic anemia.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to phenylhydrazine can cause vomiting, diarrhea, fatigue, headache, and irritation and itchiness of the eyes and skin.

2. *Long-term (chronic):* Repeated skin contact with phenylhydrazine can cause skin sensitization and eczematous dermatitis with redness, swelling, and rash.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers

for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to phenylhydrazine, the 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, liver, kidneys, and hematopoietic (blood-cell forming), nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to workers with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to phenylhydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to phenylhydrazine.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examina-

tions may be necessary should a worker develop symptoms that may be attributed to exposure to phenylhydrazine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and hematopoietic, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to phenylhydrazine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of phenylhydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting phenylhydrazine with tubes containing sulfuric-acid-coated silica and analyzing by gas chromatography. Direct-reading devices calibrated to measure phenylhydrazine may also be used if available. A detailed sampling and analytical method for phenylhydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with phenylhydrazine.

SANITATION

Clothing which is contaminated with phenylhydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of phenylhydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of phenylhydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with phenylhydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle phenylhydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to phenylhydrazine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for phenylhydrazine

Operations	Controls
During the manufacture of phenylhydrazine; during maintenance of manufacturing and storage equipment	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the manufacture of pharmaceuticals, photographic developers, polymethene dyes, and nitron (a stabilizer for explosives)	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an analytical reagent, intermediate in inorganic synthesis, or reducing agent	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to phenylhydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If phenylhydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to phenylhydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If phenylhydrazine gets on the skin, wash it immediately with soap and water. If phenylhydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If phenylhydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing phenylhydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing phenylhydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Phenylhydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulation.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for phenylhydrazine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR beta-PROPIOLACTONE POTENTIAL HUMAN CARCINOGEN

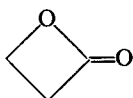
INTRODUCTION

This guideline summarizes pertinent information about beta-propiolactone for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₃H₄O₂

• **Structure:**



• **Synonyms:** 2-Oxetanone; BPL; hydracrylic acid beta-lactone; 3-hydroxypropionic acid lactone; propanolide; 1,3-propiolactone; 3-propiolactone; beta-propionolactone.

• **Identifiers:** CAS 57-57-8; RTECS RQ7350000; DOT not assigned

• **Appearance and odor:** Colorless liquid with a pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 72.06
2. Boiling point (at 760 mmHg): 162 °C (323.6 °F), decomposes
3. Specific gravity (water = 1): 1.1460
4. Vapor density (air = 1 at boiling point of beta-propiolactone): 2.5
5. Melting point: -33.4 °C (-28.12 °F)
6. Vapor pressure at 25 °C (77 °F): 3.4 mmHg
7. Solubility in water, g/100 g water at 25 °C (77 °F): 37
8. Evaporation rate (butyl acetate = 1): 0.223
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 0.45% (4,473 ppm)

• Reactivity

1. Incompatibilities: beta-Propiolactone polymerizes during storage, hydrolyzes readily in water, and decomposes if stored at room temperature.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving beta-propiolactone.
3. Caution: beta-Propiolactone can polymerize and rupture containers, especially at elevated temperatures.

• Flammability

1. Flash point: 74 °C (165 °F) (closed cup)
2. Flammable limits in air, % by volume: Lower, 2.9; upper, not available
3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
4. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

• Warning properties

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for beta-propiolactone; however, the OSHA standard requires implementation of stringent controls wherever beta-propiolactone or solid or liquid mixtures containing at least 0.1% by weight or volume of beta-propiolactone are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1013, beta-Propiolactone. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated beta-propiolactone as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV[®]) of 0.5 parts of beta-propiolactone per million parts of air (ppm) [1.5 milligrams per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration for a normal 8-hour workday or a 40-hour workweek.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• Routes of exposure

beta-Propiolactone may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• Summary of toxicology

Effects on animals: In rats, acute oral administration or intraperitoneal injection of beta-propiolactone caused muscular spasms, respiratory difficulty, convulsions, and death. Acute intravenous injection caused kidney tubule and liver damage. Subcutaneous injection of beta-propiolactone in rats and mice produced cancer at the sites of administration. Single intraperitoneal injections in suckling mice produced lymphatic tumors and liver cancer.

• Signs and symptoms of exposure

Short-term (acute): Exposure to beta-propiolactone can cause irritation and blistering of the skin, hair loss, and scarring. Eye contact with liquid beta-propiolactone can cause permanent corneal opacification.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to beta-propiolactone, the 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 con-

centrate on the function and integrity of the eyes, skin, liver, kidneys and respiratory systems. Medical surveillance for respiratory diseases should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to beta-propiolactone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic diseases of the skin or liver. The physician should obtain baseline values for liver function tests.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to beta-propiolactone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, eyes, liver, kidneys, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to beta-propiolactone may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• Method

There are no NIOSH-validated sampling and analytical methods for beta-propiolactone.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where beta-propiolactone is contained in an otherwise "closed

system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where beta-propiolactone is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower in the designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with beta-propiolactone should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of beta-propiolactone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of beta-propiolactone's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove beta-propiolactone from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1013:

Areas where beta-propiolactone is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of beta-propiolactone, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving beta-propiolactone which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of beta-propiolactone into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where beta-propiolactone is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of beta-propiolactone shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove beta-propiolactone from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to beta-propiolactone may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for beta-propiolactone

Operations	Controls
During use in the manufacture of acrylic acids and esters; during use in the sterilization of blood plasma, tissue grafts, and surgical instruments; during use in research and laboratory facilities	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker had contact with beta-propiolactone, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to beta-propiolactone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If beta-propiolactone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to beta-propiolactone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If beta-propiolactone gets on the skin, wash it immediately with soap and water. If beta-propiolactone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots,

and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If beta-propiolactone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing beta-propiolactone should be absorbed on paper towels and placed in an appropriate container.
4. Large quantities of liquids containing beta-propiolactone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing beta-propiolactone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: When engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for beta-propiolactone

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TETRAMETHYL SUCCINONITRILE

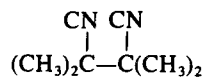
INTRODUCTION

This guideline summarizes pertinent information about tetramethyl succinonitrile (TMSN) for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₈H₁₂N₂

• **Structure:**



• **Synonyms:** Succinonitrile tetramethyl, TMSN, TSN, tetramethyl-butanedinitrile

• **Identifiers:** CAS 3333-52-6; RTECS WN4025000; DOT Not assigned

• **Appearance and odor:** Colorless and odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 136.22
2. Specific gravity (water = 1): 1.07
3. Melting point: 170°C (338°F), sublimes
4. Insoluble in water

• Reactivity

1. Incompatibilities: Strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., cyanides, oxides of nitrogen, and carbon monoxide) may be released in a fire involving TMSN.

• Flammability

1. Extinguishant: Water, dry chemical, or carbon dioxide.
2. Caution: TMSN is a combustible solid. All ignition sources must be controlled when TMSN is used, handled, or stored so as not to create a potential fire or explosion hazard.

• Warning properties

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, TMSN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for TMSN is 0.5 parts of TMSN per million parts of air (ppm) [3.0 milligrams of TMSN per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 1 ppm (6 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 0.5 ppm (3 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for tetramethyl succinonitrile

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA (Skin)*	0.5	3
NIOSH REL ceiling (15 min)	1	6
ACGIH TLV [®] TWA (Skin)	0.5	3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• Routes of exposure

TMSN may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

Effects on animals: Acute inhalation, subcutaneous injection, or oral administration of TMSN to rats, mice, or hamsters

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produced severe convulsions and death within several hours of exposure.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to TMSN can cause headache, sensation of pressure within the head, dizziness, nausea, vomiting, peculiar taste, respiratory distress, fatigue, convulsions, and unconsciousness.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to TMSN, the 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 in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to TMSN at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history and physical findings consistent with a convulsant disorder.

- **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to TMSN. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the central nervous system as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of TMSN. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting TMSN vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure TMSN may also be used if available. A detailed sampling and analytical method for TMSN may be found in the *NIOSH Manual of Analytical Methods* (method number SI55).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with solid TMSN or liquids containing TMSN.

Workers should be provided with and required to use dust- and splash-proof safety goggles where TMSN may come in contact with the eyes.

SANITATION

Clothing which is contaminated with TMSN should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of TMSN from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of TMSN's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with TMSN should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle TMSN should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to TMSN may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for tetramethyl succinonitrile

Operations	Controls
During the manufacture of polymers initiated by azobisisobutyronitrile; during the processing of products expanded with azobisisobutyronitrile	Local exhaust ventilation
During the manufacture of expanded polyvinyl chloride and polystyrene when azobisisobutyronitrile is used as a blowing agent	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to TMSN, an eye-wash fountain should be provided within the immediate work area for emergency use.

If TMSN gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible.

Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to TMSN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If TMSN gets on the skin, wash it immediately with soap and water. If TMSN penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If TMSN is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing TMSN, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from TMSN vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing TMSN may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. TMSN should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in the solid form, TMSN may be collected and placed in an appropriate container.
6. TMSN solid or liquid may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However,

there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for tetramethyl succinonitrile

Condition	Minimum respiratory protection*†
Concentration: Less than or equal to 5 ppm	Any supplied-air respirator Any self-contained breathing apparatus
Planned or emergency entry into environments containing unknown concentrations or levels above 5 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (6 mg/m³) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TOLUENE DIISOCYANATE

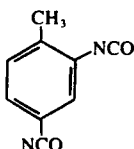
INTRODUCTION

This guideline summarizes pertinent information about toluene diisocyanate (TDI) for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₉H₆N₂O₂

• **Structure:**



• **Synonyms:** 2,4-Diisocyanato-1-methyl benzene; TDI; toluene-2, 4-diisocyanate; 2,4-toluene diisocyanate

• **Identifiers:** CAS 584-84-9; RTECS CZ6300000; DOT 2078, label required: "Poison"

• **Appearance and odor:** Colorless to pale yellow liquid with a sharp, pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 174.16
2. Boiling point (at 760 mmHg): 251°C (484°F)
3. Specific gravity (water = 1): 1.22
4. Vapor density (air = 1 at boiling point of TDI): 6.0
5. Melting point: 21°C (69.8°F)
6. Vapor pressure at 25°C (77°F): 0.05 mmHg
7. Insoluble in water (reacts exothermically)
8. Evaporation rate (butyl acetate = 1): Much less than 1
9. Saturation concentration in air (approximate) at 25°C (77°F): 0.00657% (65.7 ppm)

• Reactivity

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with water, acids, bases, and

amines may cause reactions that liberate heat and cause violent foaming and spattering.

2. Hazardous decomposition products: Toxic gases and vapors (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving TDI.

3. Caution: TDI will attack some forms of plastic, rubber, and coatings.

• Flammability

1. Flash point: 132°C (270°F) (open cup)
2. Flammable limits in air, % by volume: Lower, 0.9; upper, 9.5
3. Extinguishant: Carbon dioxide, dry chemical powder, or foam
4. Class IIIB Combustible Liquid (29 CFR 1910.106), Flammability Rating 1 (NFPA)

• Warning properties

1. Odor threshold: 0.17 ppm
2. Eye irritation levels: 0.05-0.1 ppm
3. Evaluation of warning properties for respirator selection: Because of the lack of odor and irritant effects at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), TDI can only be detected above the NIOSH REL; thus TDI is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for TDI is 0.02 parts of TDI per million parts of air (ppm) [0.14 milligrams of TDI per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.005 ppm (0.135 mg/m³) as a time-weighted average (TWA) concentration for up to a 10-hour workshift, 40-hour workweek, and the ceiling concentration is 0.02 ppm (0.14 mg/m³) as determined in any 10-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 0.005 ppm (0.04 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek, and the short-term exposure limit (STEL) is 0.02 ppm (0.15 mg/m³) (Table 1).

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Table 1.—Occupational exposure limits for toluene diisocyanate

	Exposure limits	
	ppm	mg/m ³
OSHA PEL ceiling	0.02	0.14
NIOSH REL TWA	0.005	0.035
Ceiling (10 min)	0.02	0.14
ACGIH TLV® TWA	0.005	0.04
STEL	0.02	0.15

HEALTH HAZARD INFORMATION

• Routes of exposure

TDI may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• Summary of toxicology

1. *Effects on animals:* Chronic administration of TDI by gavage to rats and mice produced cancer of the skin, pancreas, liver, mammary glands, and blood vessels. Chronic inhalation of TDI by rats caused increased fibrous tissue in the lung bronchioles, inflammation of the lungs and trachea, and death due to hemorrhage in the lungs. NIOSH will continue to monitor the research regarding TDI to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.

2. *Effects on humans:* Exposure to TDI has caused severe bronchospasm, lung inflammation, fluid in the lungs, and decreased breathing capacity. It has also caused sensitization of the respiratory tract, as manifested by acute asthmatic reaction upon return to work after a period of time away from exposure.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to TDI can cause coughing, tightness of the chest, chest pain, nausea, vomiting, abdominal pain, headache, and insomnia. TDI can also cause severe skin irritation with redness, swelling, and blistering, and eye irritation with permanent damage if untreated.

2. *Long-term (chronic):* Exposure to TDI can cause respiratory sensitization; initial symptoms include coughing during the night, with difficult or labored breathing. Skin sensitization can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to TDI, the 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 respiratory system, eyes, and skin. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to TDI at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. The physician should note that a bronchial challenge test for nonspecific airway hyperreactivity (e.g., to cold air, exercise, methacholine, or histamine) may not be sufficiently sensitive or specific for identifying workers who are susceptible or sensitized to the effects of TDI.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to TDI. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory system, eyes, and skin as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, pre- and post-shift tests of lung function, and chest X-rays. At the current state of knowledge, tests

for tolyl-specific serum IgE antibodies are not sufficiently sensitive or specific for use in medical screening or diagnosis of bronchial hypersensitivity in workers exposed to TDI.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to TDI may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Extrinsic asthma (acute).
2. Delayed-onset SHE's include: Extrinsic asthma (chronic).

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to TDI should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of TDI. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 10-minute sample or a series of consecutive samples that total 10 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

Sampling and analysis may be performed by collecting TDI vapors using midget impingers filled with a solution of 1-(2-methoxy phenyl)-piperazine in toluene and analyzing by liquid chromatography with UV detection. Detector tubes or other direct-reading devices calibrated to measure TDI may also be used if available. A detailed sampling and analytical method for TDI may be found in the *NIOSH Manual for Analytical Methods* (method number 2535).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the

manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with TDI.

Workers should be provided with and required to use splash-proof safety goggles where TDI may come in contact with the eyes.

SANITATION

Clothing which is contaminated with TDI should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of TDI from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of TDI's hazardous properties. Before being laundered, contaminated clothing shall be placed in a decontaminating solution of water containing 10% ammonia in a container that is impervious to TDI. Caution: Do not tightly close containers used for decontamination because of a possible increase in gas pressure.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with TDI should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle TDI should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to TDI may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for toluene diisocyanate

Operations	Controls
During use in the manufacture of diisocyanatepolyol surface coatings and finishes, polyurethane paints, and electrical and thermal insulation	Process enclosure, general dilution ventilation, local exhaust ventilation, personal protective equipment
During use in the manufacture and curing of flexible polyurethane foams and elastoplastics, adhesives, and sealants	Process enclosure, general dilution ventilation, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to TDI, an eye-wash fountain should be provided within the immediate work area for emergency use.

If TDI gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to TDI, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If TDI gets on the skin, wash it immediately with soap and water. If TDI penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If TDI is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing TDI, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from TDI vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing TDI may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. TDI should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing TDI may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed

to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for toluene diisocyanate

Condition	Minimum respiratory protection* †
Concentration:	
Less than or equal to 0.05 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 0.125 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 10 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 10 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.005 ppm (0.035 mg/m³) (TWA) and 0.02 ppm (0.14 mg/m³) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TRICHLOROETHYLENE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about trichloroethylene for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2HCl_3
- **Structure:** $CCl_2 = CHCl$
- **Synonyms:** Acetylene trichloride, ethylene trichloride, TCE
- **Identifiers:** CAS 79-01-6; RTECS KX455000; DOT 1710, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless liquid with a sweet odor like chloroform

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 131.38
 2. Boiling point (at 760 mmHg): 87.1°C (188°F)
 3. Specific gravity (water = 1): 1.46
 4. Vapor density (air = 1 at boiling point of trichloroethylene): 4.54
 5. Melting point: -86.4°C (-123°F)
 6. Vapor pressure at 25°C (77°F): 74.3 mmHg
 7. Solubility in water, g/100 g water at 25°C (77°F): 0.00011
 8. Evaporation rate (butyl acetate = 1): 6.2
 9. Saturation concentration in air (approximate) at 25°C (77°F): 10.1% (101,000 ppm)
 10. Ionization potential: 9.47 eV
- **Reactivity**
 1. Incompatibilities: Trichloroethylene may react violently with chemically active metals such as barium, lithium, sodium, magnesium, and titanium. Aluminum may react with the free hydrogen chloride in trichloroethylene to produce aluminum

chloride, which catalyzes a violent self-accelerating polymerization reaction. Contact with strong caustics may cause the formation of dichloroacetylene, a toxic and flammable gas.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., phosgene, hydrogen chloride, and carbon monoxide) may be released in a fire involving trichloroethylene.

- **Flammability**

1. Flash point: 32°C (90°F) (closed cup)
2. Autoignition temperature: 788°C (420°F)
3. Flammable limits in air, % by volume: Lower, 12.5; Upper, 90
4. Extinguishant: Alcohol foam, dry chemical, or carbon dioxide
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 1, Practically Nonflammable (NFPA)

- **Warning properties**

1. Odor threshold: 21.4 ppm
2. Eye irritation level: 400 ppm
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for trichloroethylene per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 200 ppm; and the maximum peak concentration above the acceptable ceiling (maximum duration of 5 minutes in any 2-hour period) is 300 ppm. The National Institute for Occupational Safety and Health (NIOSH) recommends that trichloroethylene be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV[®]) is 50 ppm (270 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 200 ppm (1,080 mg/m³) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for trichloroethylene

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	100	—
Acceptable ceiling	200	—
Maximum ceiling (5 min in 2 h)	300	—
NIOSH REL TWA (Ca)*	25	—
ACGIH TLV [®] TWA	50	270
STEL	200	1,080

* (Ca): NIOSH recommends treating as a potential human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Trichloroethylene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of trichloroethylene by multiple species of animals caused depressed brain function, brain damage, liver and kidney injury, and death due to respiratory failure or cardiac arrest. In rats, rabbits, guinea pigs, and gerbils, chronic inhalation of trichloroethylene caused toxic effects on the nerves, increases in liver and kidney weights, and suppression of growth. Chronic oral administration of trichloroethylene to mice produced cancers of the liver and lungs, and chronic inhalation by female mice produced cancers of the lymph system and lungs.

2. *Effects on humans:* Acute inhalation or ingestion of trichloroethylene has caused reversible peripheral nerve degeneration, injury to the liver and kidneys and to the cardiovascular and gastrointestinal systems, depression of the central nervous system, coma, and sudden death due to respiratory failure, cardiac arrhythmia, or liver or kidney failure. Chronic exposure to trichloroethylene has caused damage to the liver, kidneys, and nervous system. The ingestion of alcohol, caffeine, and some prescription drugs has been found to potentiate the effects of trichloroethylene intoxication. A dermal response seen as a reddening of the face, neck, back, and shoulders (degreaser's flush) has occurred in chronically exposed workers following the ingestion of alcohol. Repeated immersion of the hands into liquid trichloroethylene has caused paralysis of the fingers.

• Signs and symptoms of exposure

1. *Short-term (acute):* Inhalation exposure to trichloroethylene can cause drowsiness, dizziness, headache, blurred vision, incoordination, mental confusion, flushed skin, tremors, nausea, vomiting, fatigue, and cardiac arrhythmia. Irritation of the skin, mucous membranes, and eyes can also occur.

2. *Long-term (chronic):* Exposure can cause headache, cough, double vision, impaired coordination and senses of touch and smell, anxiety, dizziness, giddiness, weakness, tremor, slowness of heartbeat, and intolerance to alcohol. Dryness of the skin, blisters, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, and morbidity and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to trichloroethylene, the 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, liver, kidneys, and cardiovascular, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to trichloroethylene at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin or liver. The physician should obtain baseline values for liver function tests.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that

may be attributed to exposure to trichloroethylene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and cardiovascular, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to trichloroethylene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to trichloroethylene should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting trichloroethylene vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure trichloroethylene may also be used if available. A detailed sampling and analytical method for trichloroethylene may be found in the *NIOSH Manual of Analytical Methods* (method number S336).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with trichloroethylene.

SANITATION

Clothing which is contaminated with trichloroethylene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of trichloroethylene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of trichloroethylene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with trichloroethylene should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle trichloroethylene should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to trichloroethylene may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for trichloroethylene

Operations	Controls
During use as a cleaning solvent in cold cleaning and vapor degreasing operations	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a scouring and cleaning agent in textile processing; during use in the extraction and purification of animal and vegetable oils in food and pharmaceutical industries; during use in chemical synthesis	Process enclosure, local exhaust ventilation
During use in the manufacture of adhesives, anesthetics and analgesics, and cleaning and polishing preparations	Process enclosure, local exhaust ventilation
During use as a fumigant and disinfectant for seeds and grains	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to trichloroethylene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If trichloroethylene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to trichloroethylene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If trichloroethylene gets on the skin, wash it immediately with soap and water. If trichloroethylene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If trichloroethylene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing trichloroethylene, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing trichloroethylene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. Liquids containing trichloroethylene may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should

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Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for trichloroethylene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR VINYL CHLORIDE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about vinyl chloride for workers, employers, and 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; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C₂H₃Cl
- **Structure:** CH₂=CHCl
- **Synonyms:** Chlorethene, chlorethylene, monochlorethylene, chloroethylene
- **Identifiers:** CAS 75-01-4; RTECS KU9625000; DOT 1086, label required: "Flammable Gas"
- **Appearance and odor:** Colorless gas with a sweet odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 62.50
 2. Boiling point (at 760 mmHg): -14°C (7°F)
 3. Specific gravity (water = 1): 0.9121
 4. Vapor density (air = 1 at boiling point of vinyl chloride): 2.15
 5. Melting point: -155.7°C (-243.4°F)
 6. Vapor pressure at 20°C (68°F): 2,580 mmHg
 7. Solubility in water, g/100 g water at 24°C (75°F): 0.11
 8. Ionization potential: 9.995 eV
- **Reactivity**
 1. Incompatibilities: Atmospheric oxygen and strong oxidizers may react with vinyl chloride to produce peroxide, which can initiate a violent polymerization reaction.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride and carbon monoxide) may be released in a fire involving vinyl chloride.
3. Caution: Check valves for leaks.

• Flammability

1. Flash point: -78°C (-108°F) (open cup)
2. Autoignition temperature: 472°C (882°F)
3. Flammable limits in air, % by volume: Lower, 3.6; Upper, 33.0
4. Class IA Flammable Liquid Gas (29 CFR 1910.106), Flammability Rating 4 (NFPA)

• Warning properties

1. Odor threshold: 3,000 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for vinyl chloride is 1 part of vinyl chloride per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift, and the ceiling concentration which shall at no time be exceeded is 5 ppm as determined in any 15-minute sampling period. The National Institute for Occupational Safety and Health (NIOSH) recommends that vinyl chloride be controlled and handled as a potential human carcinogen in the workplace, and the NIOSH recommended exposure limit (REL) is that exposure be minimized to the lowest feasible limit. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated vinyl chloride as an A1 substance (suspected human carcinogen) with an assigned threshold limit value, TLV[®] of 5 ppm [10 milligrams of vinyl chloride per cubic meter of air (mg/m³)] as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for vinyl chloride

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	1	—
Ceiling (15 min)	5	—
NIOSH REL (Ca)*	Lowest feasible limit	
ACGIH TLV [®] TWA (Ala)†	5	10

* (Ca): NIOSH recommends treating as a potential human carcinogen.

† (Ala): Human carcinogen with an assigned TLV.

HEALTH HAZARD INFORMATION

• Routes of exposure

Vinyl chloride may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of vinyl chloride by multiple species of animals caused central nervous system depression, coma, and death; acute inhalation by dogs also caused cardiac arrhythmias. In mice, rats, and hamsters, chronic inhalation or oral administration of vinyl chloride produced cancers of the liver, kidney, central nervous system, skin, and mammary and ear duct glands.

2. *Effects on humans:* Acute exposure of workers to vinyl chloride has caused narcotic and anesthetic effects. Repeated exposure of workers to vinyl chloride has caused increased blood pressure, decreased blood platelet counts, increased liver enzyme levels, restricted blood flow, bone degeneration in the fingers, liver and spleen enlargement, nervous system disturbances, central nervous system depression, decreased respiratory function, and emphysema. Cancer of the liver has been associated with exposure of workers to vinyl chloride during the polyvinyl chloride production process. Cancers of the lung, brain, skin, nervous system, gall bladder, mouth, and pharynx have also been observed in workers with a history of exposure to vinyl chloride. An increase in fetal mortality has been reported among wives of workers who had been exposed to vinyl chloride.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to vinyl chloride can cause dizziness, light-headedness, nausea, dullness of visual and auditory responses, drowsiness, and unconsciousness. Irritation of the skin and eyes can also occur. Skin contact with the liquid can cause frostbite.

2. *Long-term (chronic):* Exposure to vinyl chloride can cause thickening of the skin, contact and allergic dermatitis, fatigue, coughing and sneezing, abdominal pain, gastrointestinal bleeding, nausea, vomiting, indigestion, diarrhea, jaundice, weight loss, anorexia, and a cold and tingling sensation of the hands and feet.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) 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 surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including the employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to vinyl chloride, the 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 skin, liver, kidneys, and cardiovascular, hematopoietic (blood cell forming), nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to vinyl chloride. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver. The physician should obtain baseline values for serological tests of liver function and markers for infection with Hepatitis B virus.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations

should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to vinyl chloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, kidneys, and cardiovascular, hematopoietic, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following test should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and test of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which 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 to those expected for a suitable reference population. Because occupational exposure to vinyl chloride may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

Delayed-onset SHE's include: Liver cancer (hemangiosarcoma) and "white finger" (Raynaud's syndrome, secondary to vasculitis)

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting vinyl chloride vapors with tandem charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure vinyl chloride may also be used if available. A detailed sampling and analytical method for vinyl chloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1007).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with vinyl chloride.

SANITATION

Clothing which is contaminated with vinyl chloride should be removed immediately and placed in sealed containers for

storage until it can be discarded or until provision is made for the removal of vinyl chloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of vinyl chloride's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with vinyl chloride should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle vinyl chloride should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to vinyl chloride may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for vinyl chloride

Operations	Controls
During the manufacture of monomer, polymer, copolymer, and terpolymer	Process enclosure, personal protective equipment
During the transfer of monomer to tank cars or polymerization reactors; during maintenance work on tanks or reactors	Local exhaust ventilation, personal protective equipment
During the cleaning of polymerization reaction tanks	Process enclosure, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures:

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to vinyl chloride, an eye-wash fountain should be

provided within the immediate work area for emergency use.

If vinyl chloride gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to vinyl chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If vinyl chloride gets on the skin, wash it immediately with soap and water. If vinyl chloride penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If vinyl chloride is spilled or leaked, the following steps should be taken:

1. Stop the flow of gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted canister providing protection against the compound of concern Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.