

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** CYCLOHEXANONE ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for CYCLOHEXANONE

Basic text of this document contains the draft technical standard
developed by the Joint Review Committee of the NIOSH/OSHA Standards
Development Program and the supporting documentation for the substance
CYCLOHEXANONE.

SCP draft technical standards are recommendations to the Department of
Health, Education and Welfare for its consideration in rulemaking and have no legal status until
final rules have been promulgated by that agency. This draft standard is
provided for your information only.

References and Sources, Respirator Table Documentation and Use/Exposure
Control Documentation are the working documents used by the various SCP
working groups during the development of the draft technical standard and
serve as the technical foundation for the standard. The classification for
the substance and the regulatory statements were derived following a
rationale logic established for the various sections of the standard.

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DEFINITIONS

PERMISSIBLE EXPOSURE - "Permissible Exposure" means inhalation of cyclohexanone in concentrations not in excess of 50 parts per million (ppm) (200 milligrams per cubic meter, mg/cu.m.) averaged over an 8-hour work shift, as stated in section 1910.93, Table G-1.

ACTION LEVEL - "Action Level" means one half (1/2) of the permissible exposure for cyclohexanone.

EMPLOYEE INFORMATION - Each employer who has a workplace in which cyclohexanone is present shall:

STANDARD AVAILABILITY - Keep a copy of this section with its appendices at the workplace. This material shall be made readily available to affected employees; and

PRESENCE OF CYCLOHEXANONE - Inform affected employees of the quantity, location, and manner of use or storage of cyclohexanone.

EXPOSURE MEASUREMENT

INITIAL DETERMINATION - Each employer who has a place of employment in which cyclohexanone is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of cyclohexanone at or above the action level. The determination shall be made each time there is a change in production, process, or control measures which could result in an increase in airborne concentrations of cyclohexanone. A written determination shall be made and it shall contain at least the following information:

- (i) Any information, observations, or calculations which would indicate employee exposure to cyclohexanone;
- (ii) Any measurements of airborne concentrations of cyclohexanone taken;
- (iii) Any employee complaints of symptoms which may be attributable to exposure to cyclohexanone; and
- (iv) Date of determination, work being performed at the time, location within work site, name, and social security number of each employee considered.

INITIAL EXPOSURE MEASUREMENT - If the employer determines that any employee may be exposed to airborne concentrations of cyclohexanone at or above the action level, the exposure of the employee believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum exposure of the employee.

IDENTIFICATION OF EXPOSED EMPLOYEES - If the exposure measurement taken under paragraph (c)(2) of this section reveals employee exposure to airborne concentrations of cyclohexanone at or above the action level, the employer shall:

- (i) Identify all employees who may be exposed at or above the action level; and
- (ii) Measure the exposure of the employees so identified.

EXPOSURE ABOVE THE ACTION LEVEL - If an employee exposure measurement reveals that an employee is exposed to airborne concentrations of cyclohexanone at or above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every two months.

EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE - If an employee exposure measurement reveals that an employee is exposed to airborne

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concentrations of cyclohexanone above the permissible exposure, the employer shall:

- (i) Inform the employee of the exposure as required by paragraph (N)(1) of this section; and
- (ii) Measure the exposure of the employee at least monthly; and
- (iii) Institute control measures as required by paragraph (E) of this section.

TERMINATION OF EXPOSURE MEASUREMENT - If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to airborne concentrations of cyclohexanone below the action level, the employer may terminate measurement for the employee. For purposes of this subparagraph, use of respirators shall not constitute reduction of employee exposure below the action level.

METHODS OF MEASUREMENT - An employee's exposure shall be obtained by combination of long term or short term samples which represents the employee's actual exposure averaged over an eight hour work shift (Appendix B (iv)). The method of measurement shall have an accuracy, to confidence level of 95%, of not less than that given in Table 1 below.

Table 1

Concentration	Required Accuracy
permissible exposure	Plus or Minus 25%
below permissible exposure	
above the action level	Plus or Minus 35%
below the action level	Plus or Minus 50%

Methods of Compliance

Engineering controls - No employee shall be exposed to cyclohexanone above the permissible limit as defined in paragraph (a)(1) of this section. Engineering and work practice controls shall be used to reduce exposure to cyclohexanone to at or below the permissible exposure.

- (i) When mechanical ventilation is used to control exposure, measurements which demonstrate system efficiency (for example: air velocity, static pressure, or air volume) shall be made at least every three months. Measurements of system efficiency shall also be made within five work days of any change in production, process, or control which might result in a reduction in control.
- (ii) Where a fan is located in duct work and where cyclohexanone is present in concentrations greater than 2750 ppm, one fourth of the lower flammable limit, the fan rotating element shall be of nonsparking material or the casing shall consist of, or be lined with, nonsparking material. There shall be sufficient clearance between the fan rotating element and the fan casing so as to prevent contact.
- (iii) In the design of open surface tank ventilation for the purposes of compliance with section 1910.94(d), operations involving cyclohexanone shall be classified as B-4 at 70 F.

Respirators

- (i) Compliance with the permissible exposure may not be achieved by the use of respirators except:

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- (a) During the time period necessary to install engineering controls; or
- (b) In work situations in which engineering controls are technically not feasible; or
- (c) In work situations in which feasible engineering and work practice controls are insufficient to reduce employee exposure to at or below the permissible exposure. Where technically feasible engineering and work practice controls are not sufficient to reduce exposure to at or below permissible exposure, they shall be used to reduce exposure to the lowest level feasible; or
- (d) For operations not exceeding 40 hours per year; or
- (e) In emergencies.

(ii) Respirators shall be jointly approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) and by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.

(iii) Employers shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.

(iv) Employers shall institute a respiratory protection program in accordance with sections 1910.134(b),(d),(e),(f) and (g).

TABLE 2. RESPIRATORY PROTECTION FOR CYCLOHEXANONE

Concentration	Permissible Respiratory Protection
to or Less 1000 ppm	a full facepiece and organic vapor cartridge(s).
to or Less 500 ppm	organic vapor canister. Any supplied-air respirator with a full facepiece. Any self-contained breathing apparatus with a full facepiece.
to or Less 100 ppm	operated in pressure-demand (positive pressure) mode or with a full facepiece, hood, or helmet operated in continuous flow mode.
greater than 100 ppm, or entry into confined space from	Self-contained breathing apparatus with a full face- piece operated in pressure-demand (positive pressure)

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in concentra-	A combination respirator which includes a type C supplied air-respirator with a full facepiece operated in pressure-demand (positive pressure) or continuous flow mode and an auxiliary self-contained air supply operated in pressure-demand mode.
ighting	Self-contained breathing apparatus with a full face-piece operated in pressure-demand (positive pressure) mode.
	Any escape self-contained breathing apparatus. Any gas mask providing protection against organic vapors.

Fire and Safety

Employers shall familiarize themselves with the information contained in Substance Technical Guidelines for cyclohexanone which is contained in Appendix B in order to ensure the safe handling and use of cyclohexanone.

Electrical - For the purposes of compliance with section 1910.309, locations classified as hazardous locations due to the presence of cyclohexanone shall be Class I Group D.

Portable fire extinguishers - For the purposes of compliance with section 1910.157, cyclohexanone is classified as a Class B fire hazard.

Powered industrial trucks - For the purposes of compliance with section 1910.178, locations classified as hazardous locations due to the presence of cyclohexanone shall be Class I Group D.

Combustible liquids - For the purposes of compliance with section 1910.106, liquid cyclohexanone is classified as a Class II combustible liquid. Spray finishing operations shall be performed in accordance with sections 1910.107 and 1910.94(c). Dip tank operations shall be performed in accordance with sections 1910.108 and 1910.94(d).

Sources of ignition - Sources of ignition such as smoking and open flames are prohibited where cyclohexanone is used, handled or stored in a manner so as to create a potential fire or explosion hazard.

Personal Protective Equipment

Skin Contact

- (i) Employers shall provide, and require employees to use, impervious clothing, gloves, face shields (8 inch minimum) and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact to cyclohexanone. Face shields shall comply with section 1910.133(a)(6).
- (ii) Employers shall ensure that clothing contaminated with cyclohexanone is placed in closed containers. Employers shall provide for the cleaning or disposal of such clothing and if the clothing is to be laundered or otherwise cleaned, shall inform the person performing this operation of the hazardous properties of cyclohexanone.

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- (iii) Employers shall ensure that non-impervious clothing which becomes wet with cyclohexanone be removed promptly and not reworn until the cyclohexanone is removed from the clothing.
- (iv) Employers shall ensure that clothing which becomes wet with cyclohexanone be removed immediately and not reworn until the cyclohexanone is removed from the clothing.

Eye Contact

- (i) Employers shall provide, and require employees to use, splash-proof safety goggles (cup-cover type dust and splash safety goggles), which comply with section 1910.133(a)(6), where eye contact to liquid cyclohexanone may occur.

Spills

Spills of cyclohexanone shall be cleaned up immediately after eliminating potential sources of ignition and utilizing available ventilation.

Liquid cyclohexanone may not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

Sanitation

Employers shall ensure that employees whose skin becomes wet with cyclohexanone promptly wash or shower as necessary to remove any cyclohexanone from the skin.

Where skin contamination may occur and showers are required for adequate cleaning of the body, employers shall provide showers as described in section 1910.141(d)(3).

Training and Information - Each employer who has employees exposed to cyclohexanone in excess of the action level, or employees who may have skin or eye contact with liquid cyclohexanone, or employees who work in the area of accidental release, spill, fire, or explosion of cyclohexanone may be required to provide training annually:

Substance Safety Data Sheet - Inform each employee of the information contained in the Substance Safety Data Sheet for cyclohexanone, which is contained in Appendix A; and

Medical -

- (I) Advise employees as to the signs and symptoms of exposure to cyclohexanone.
- (II) Instruct the employees to advise the employer of the development of signs and symptoms of exposure to cyclohexanone which are listed in Appendix A.
- (III) Instruct the employees to inform the employer if they develop any of the medical conditions listed in (k)(2) of this section; and

Procedures -

- (I) Provide training to insure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to cyclohexanone.
- (II) The procedures required by (j)(1), (2), and (3)(I) shall be provided to employees at the expense of the employer during the employee's normal working hours. (k) Medical Surveillance

The employer shall provide medical procedures as required by paragraph (k). These procedures shall be provided at no cost to the employee.

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Preplacement Questionnaire - The employer shall obtain from each employee who will be exposed to liquid cyclohexanone, or airborne concentrations of cyclohexanone at or above the action level, a written statement whether such employee has a history of any of the following:

- (i) Liver disease
- (ii) Chronic lung disease
- (iii) Skin disease
- (iv) Kidney disease

Preplacement Medical Examination - The employer shall provide a full examination for an employee if the employee provides a history of the conditions named in paragraph (k)(2).

Results of Preplacement Examination - The employer shall obtain a physician's written opinion based on the medical examination pursuant to paragraph (k)(3).

Periodic Medical Examinations - The employer shall provide a medical examination for an employee if the employee advises the employer of the development of:

- (i) any of the medical conditions listed in (k)(2),
- (ii) signs and symptoms listed in appendix A which the employee states may be caused by exposure to cyclohexanone.

Results of Periodic Examinations - The employer shall obtain a physician's written opinion based on the medical examination pursuant to paragraph (k)(5).

Exclusion or Removal from Exposure - No employee shall be exposed to cyclohexanone if such exposure could place the employee at increased risk of serious impairment of his health.

Emergency Procedures - The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured with exposure to cyclohexanone.

Informing the Physician - The employer shall provide to the examining physician the following information:

- (i) A copy of this regulation for cyclohexanone;
- (ii) A description of the employee's duties as they relate to his exposure to cyclohexanone;
- (iii) A description of any personal protective equipment required to be used;
- (iv) The results of any employee's exposure measurement, if available;
- (v) The employee's anticipated exposure level; and
- (vi) Upon request of the physician, information from previous full examination of the employee.

Physician's Written Opinion -

(i) The physician's written opinion shall be a signed statement of the examining physician specifically stating:

- (a) Whether the employee has any detected medical conditions which could be directly or indirectly aggravated by exposure to cyclohexanone or which could significantly interfere with the ability of the employee to follow recommended or required procedures for protecting himself from unusual or emergency exposure.
- (b) Any recommended limitations upon the employee's exposure to cyclohexanone.

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(c) The employee has been informed by the physician of any medical conditions which require further medical examination or treatment.

(ii) The written opinion shall not reveal medical information related to exposure to cyclohexanone.

(d) Refusal to be Medically Examined - If an employee refuses any required medical examination, the employer shall inform the employee of the possible health consequences of such refusal and obtain a signed statement from the employee indicating that the employee understands the risks involved by refusing to be examined.

Recordkeeping.

Initial determination.

(i) The employer shall keep an accurate record of all initial determinations required to be made pursuant to paragraph (c)(1) of this section.

(ii) The record shall include the written determination and any supporting documentation as required in paragraph (c)(1) of this section.

(iii) This record shall be maintained for at least one year.

Exposure measurements.

(i) The employer shall keep an accurate record of all measurements taken to determine employee exposure to cyclohexanone.

(ii) This record shall include:

(a) The date of measurement;

(b) A reference to the subparagraph of this regulation which required the measurement, if any;

(c) Operations involving exposure to cyclohexanone which are being monitored;

(d) Sampling and analytical methods used and evidence of their accuracy;

(e) Number, duration, and results of samples taken;

(f) Name, Social Security number, and exposure of the employee monitored.

(iii) This record shall be maintained for one year.

Mechanical ventilation.

(i) When mechanical ventilation is used as an engineering control, the employer shall maintain a record of measurements demonstrating the effectiveness of such ventilation as required by paragraph (e)(1)(i) of this section.

(ii) This record shall include:

(a) Date of measurement;

(b) Type of measurement taken;

(c) Result of measurement.

(iii) This record shall be maintained for one year.

Training and information.

(i) The employer shall keep an accurate record of all employee training and advice required by paragraph (j) of this section.

(ii) The record shall include:

(a) Date of training;

(b) Name and Social Security number of employees trained;

(c) Substance of training provided.

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(iii) This record shall be maintained for at least one year.

Medical records.

- (i) The employer shall keep an accurate medical record for each employee.
- (ii) The record shall include:
 - (a) Physician's written opinion;
 - (b) Preplacement questionnaire;
 - (c) Any employee medical complaints relative to exposure to cyclohexanone;
 - (d) A signed statement of any refusal to be examined;
 - (e) A copy of information provided to the physician pursuant to paragraph (k)(9) of this section.
- (iii) This record shall be maintained for the duration of the employment of the affected employee.

Access to records.

- (i) All records required to be maintained by this section shall be made available upon request to authorized representatives of the Assistant Secretary and the Director.
- (ii) Employee exposure measurement records required to be maintained by this section shall be made available to employees and former employees and their designated representatives.
- (iii) Employee medical records required to be maintained by this section shall be made available upon written request to a physician designated by the employee or former employee.

Observation of monitoring.

Duty.

The employer shall give affected employees or their representatives an opportunity to observe any monitoring of employee exposure to cyclohexanone which is conducted pursuant to this section.

Exercise of opportunity to observe monitoring.

- (i) When observation of the monitoring of employee exposure to cyclohexanone requires entry into an area where the use of personal protective devices is required, the observer shall use such equipment and comply with all other applicable safety procedures.
- (ii) Without interfering with the measurement, observers shall be entitled to:
 - (a) Receive an explanation of the measurement procedures;
 - (b) Visually observe all steps related to the measurement of exposure to cyclohexanone that are being performed at the place of exposure.
 - (c) Record the results obtained.

Employee notification.

The employer shall notify in writing, within five work days, every employee who is found to be exposed to cyclohexanone above the permissible exposure. The employee shall also be notified of the level of his exposure and the corrective action being taken to reduce the exposure to at or below the permissible exposure.

Pursuant to paragraph (k) of this Section, when an employee is medically examined the employer shall provide the employee with a copy of the physician's written opinion.

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APPENDIX A

SUBSTANCE SAFETY DATA SHEET

SUBSTANCE IDENTIFICATION

STANCE: Cyclohexanone
MISSIBLE EXPOSURE: 50 parts of cyclohexanone vapor per million parts of air (ppm) or 200 milligrams of cyclohexanone vapor per cubic meter of air (mg/cu m).
ARANCE AND ODOR: Colorless or slightly yellow liquid with a peppermint-like odor.

HEALTH HAZARD DATA

Ways in Which the Chemical Affects Your Body: Cyclohexanone can affect your body if it is inhaled or if it comes in contact with your skin or eyes. It may also affect your body if you swallow it.

Effects of Overexposure:

1. Short-Term Effects: Cyclohexanone may cause irritation of the eyes, nose, and throat. It may also cause dizziness and unconsciousness.
2. Long-Term Effects: Prolonged or repeated exposure of the skin to cyclohexanone can cause a rash.
3. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms associated with cyclohexanone exposure.

EMERGENCY FIRST AID PROCEDURES

Eye Exposure: If cyclohexanone gets into your eyes, wash your eyes immediately with large amounts of water, 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: If cyclohexanone gets on your non-impervious clothing or skin remove and clean the contaminated clothing and flush the contaminated skin with water promptly. When there is skin irritation, get medical attention.

Breathing: If you or any other person breathes in large amounts of cyclohexanone remove the exposed person to fresh air at once. When breathing is difficult, properly trained personnel may assist the affected person by administering oxygen. If breathing has stopped,

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perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

Swallowing: When cyclohexanone has been swallowed get medical attention immediately. If medical attention is not immediately available get the affected person to vomit by having him touch the back of his throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water). Never try to make an unconscious person vomit.

Rescue: Move affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty yourself. Understand your emergency rescue procedures and know the locations of the equipment before the need arises.

RESPIRATORS AND PROTECTIVE CLOTHING

RESPIRATORS: Respirators are not the best way to control exposure to cyclohexanone. You can only be required to wear them for routine use if your employer is in the process of installing controls or other control measures prove inadequate. You may be required to wear respirators for non-routine activities or in emergencies. If respirators are worn, they must have a Mining Enforcement and Safety Administration (MESA)/National Institute for Occupational Safety and Health (NIOSH) approval label. (Older respirators may have a Bureau of Mines approval label.)

If you can smell cyclohexanone while wearing a respirator, the respirator is not working correctly; go immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.

PROTECTIVE CLOTHING: You must wear impervious clothing, gloves, face shield, and other appropriate protective clothing over any parts of your body that could repeatedly be exposed to cyclohexanone liquid.

EYE PROTECTION: You must wear splash-proof safety goggles if it is possible that cyclohexanone may get into your eyes.

PRECAUTIONS FOR SAFE USE, HANDLING, AND STORAGE

Cyclohexanone is a combustible liquid and must be stored in tightly sealed containers, in a cool well-ventilated area, away from ignition sources. You must not smoke in areas where cyclohexanone is stored, handled, or used. Metal cyclohexanone storage containers must be grounded and bonded when transferring liquids and must be opened and closed with non-sparking tools. If your clothing becomes wet with cyclohexanone, you must remove the clothing and not wear it again until cyclohexanone has been removed. If your skin becomes wet with cyclohexanone, you must wash or shower promptly. Fire extinguishers, if provided, must be readily available and you should know where they are and how to operate them. Ask your supervisor where cyclohexanone is located in your work area and for any additional plant safety rules.

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APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
CYCLOHEXANONE

PHYSICAL AND CHEMICAL DATA

Substance Identification

1. Synonyms: Pimelic ketone; cyclohexyl ketone
2. Formula: C6H10O

Physical Data

1. Boiling point (760 mm Hg): 156.7 C (314 F)
2. Specific gravity (water=1): 0.95
3. Vapor density (air=1): 3.4
4. Melting point: -47 C (-52.6 F)
5. Vapor pressure at 20 C (68 F): 2 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): 15
7. Evaporation rate (butyl acetate=1): 0.23
8. Appearance and odor: Water white to slightly yellow liquid. Peppermint-like odor.

FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

Fire

1. Flash point: 43.9 C (111 F) (closed cup)
2. Autoignition temperature: 420 C (788 F)
3. Flammable limits in air, % by volume: Lower: 1.1 at 100 C (212 F)
4. Extinguishing media: Alcohol foam, dry chemical, or carbon dioxide.
5. Special fire-fighting procedures: Do not use solid stream of water, since stream will scatter and spread fire. Use water spray to keep containers cool.
6. Unusual fire and explosion hazards: cyclohexanone is a combustible liquid. Its vapors can form explosive mixtures in air at elevated temperatures. All ignition sources must be controlled when cyclohexanone is used, handled, and stored. Cyclohexanone vapors are heavier than air; thus the vapors may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which the cyclohexanone is handled.
7. For purposes of conforming to the requirements of 29 CFR 1910.106, cyclohexanone is classified as a Class II combustible liquid. At 2750 ppm, one fourth of the lower flammable limit, cyclohexanone is considered to be a potential fire and explosion hazard.
8. For the purposes of complying with 29 CFR 1910.309, the classification of hazardous locations as described in Article 500 of the National Electrical Code for cyclohexanone shall be Class I, Group D.

Reactivity

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1. Conditions contributing to instability: heat
2. Incompatibilities: Contact with oxidizing agents (especially nitric acid) may cause fire and explosions.
3. Hazardous Decomposition Products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclohexanone.
4. Special Precautions: cyclohexanone will attack and dissolve most plastics, resins, and rubbers.

SPILL AND LEAK PROCEDURES

If cyclohexanone 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, absorb on paper towels. Evaporate in a safe place (such as a fume hood) and burn the paper. For large quantities, can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid. Cyclohexanone may not be allowed to enter a confined space,

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

Waste Disposal Methods:

Cyclohexanone may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a sanitary land fill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid.

MONITORING AND MEASUREMENT PROCEDURES

EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken in a fashion such that the average 8-hour exposure may be determined from a single sample or two (2) 4-hour samples. Short term interval samples (up to 30 minutes) may also be used to determine average exposure level if a minimum of five (5) measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random equal duration samples taken on one (1) work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR Part 84, portable direct-reading instruments gas and vapor adsorption tubes with subsequent chemical analyses, dosimeters or with continuous monitoring system that can sample and analyze those areas most likely to represent the highest airborne concentration of cyclohexanone where employees are exposed. The method of measurement must determine the concentration of cyclohexanone to plus or minus 35%.

EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring under this section should be essentially the same as described in paragraph IV.

A. Laboratories performing chemical analyses should be accredited

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in Industrial Hygiene Chemistry by the American Industrial Hygiene Association (AIHA). The method of measurement must determine the concentration of cyclohexanone to plus or minus 25%. Methods meeting these accuracy requirements are available in the "NIOSH Monitoring Methods Manual".

MISCELLANEOUS PRECAUTIONS

High exposures to cyclohexanone can occur when transferring the liquid from one container to another.

Non-sparking tools must be used to open and close metal cyclohexanone containers which must then be effectively grounded and bonded prior to pouring.

Store cyclohexanone in tightly closed containers in a cool well ventilated area away from ignition sources.

Employers must advise employees of all plant areas and operations where exposure to cyclohexanone could occur.

COMMON OPERATIONS

Common operations in which exposure to cyclohexanone is likely to occur are use as a solvent for many inks, coatings, plastics, pesticides, explosives (RDX), as a lubricating oil additive, and as an intermediate in a commercial process for the manufacture of nylon 6.

such as a sewer, because of the possibility of an explosion.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

Route of Entry

inhalation; insignificant skin absorption

Toxicology

There may be marked local irritation of the eyes and mucous membranes at relatively low levels of exposure to cyclohexanone, and central nervous system depression may occur on exposure to high concentration, producing narcosis. Skin effects from the defatting action could occur. No chronic effects reported in humans.

Signs and Symptoms

Irritation of eyes and mucous membranes of upper respiratory tract; headache; narcosis leading to coma may occur at sustained high levels. Extensive skin contact may produce a dermatitis.

Special Tests

None in common usage.

Treatment

None specific. Remove from exposure, give artificial resuscitation if indicated, and wash eyes and contaminated skin. Recovery is usually rapid and complete.

Surveillance and Preventive Considerations

General

Most reported effects of cyclohexanone are caused by its irritant properties. It is important that the physician become familiar with plant operating conditions in which exposure to cyclohexanone occurs. Those with skin disease may not tolerate the wearing of protective clothing and those with chronic respiratory disease may not tolerate the wearing of negative pressure respirators.

Preplacement

Routine medical histories and physical examinations are not required. However the employer must screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. Renal disease -- Although cyclohexanone is not known as a kidney toxin, the importance of the organ in the elimination

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of toxic substances and metabolites justifies special consideration in those with possible impairment of renal function.

2. Chronic respiratory disease -- In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclohexanone might cause exacerbation of symptoms due to irritant properties or psychic reflex bronchospasm.
3. Liver disease -- Although cyclohexanone is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.
4. Skin disease -- Cyclohexanone is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of cyclohexanone.

Periodic Examinations

Routine periodic examinations are not required. However, if the employer becomes aware of an employee with the above listed conditions, he must refer such employee for further medical examination.

References

Browning, Ethel: Toxicity and Metabolism of Industrial Solvents, Elsevier Publishing Company, Amsterdam, 1965, pp. 443-445.

American Industrial Hygiene Association: Cyclohexanone, Hygienic Series, November-December, 1965.

Patty, F.A.: Industrial Hygiene and Toxicology, Volume II - Toxicology, Interscience Publishers, New York, 1962, pp. 1765-1768.

Grant, W. Morton: Toxicology of the Eye, Charles C. Thomas, Springfield, 1962, p. 159.

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REFERENCES AND SOURCES
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1910.93

Personal Protective Equipment, and (h) Sanitation

Eye: "Cyclohexanone," AIHA Hygienic Guide Series; Patty, "Industrial Hygiene and Toxicology;" Grant, "Toxicology of the Eye;" Carpenter and Smyth, "Chemical Burns of the Rabbit Cornea," Am. J. Ophth., 29, 1363-72 (1946)

Skin: Deichmann and Gerarde, "Toxicology of Drugs and Chemicals;" "Cyclohexanone," Union Carbide Corporation; Treon et al., "The Physiological Response of Rabbits to Cyclohexane, Methylcyclohexane, and Certain Derivatives of These Compounds," J. of Ind. Hy. and Tox., 25 (6), 199 (1943); Patty, "Industrial Hygiene and Toxicology"

Ingestion: "Cyclohexanone," Union Carbide Corporation; Browning, "Toxicity and Metabolism of Industrial Solvents;" Thienes and Haley, "Clinical Toxicology;" Patty, "Industrial Hygiene and Toxicology;" Treon et al., "The Physiological Response of Rabbits to Cyclohexane, Methylcyclohexane and Certain Derivatives of These Compounds," J. of Ind. Hy. and Tox., 25 (6), 199 (1943)

COMMENTS

Eye - Classification: 2

Output statement numbers: 10

Exceptions: None

The Hygienic Guide Series notes "small droplets (0.005 ml) of undiluted cyclohexanone placed in the eyes of rabbits caused marked irritation and some corneal injury." Patty adds, "liquid cyclohexanone may be expected to cause marked irritation with possibly some transient corneal injury when in contact with the human eye." Grant states, "testing by application of the liquid to rabbit eyes causes moderate temporary injury, graded 5 scale of 10 after 24 hours." According to Carpenter and Smyth, grade 5 indicates that 0.005 ml undiluted causes less than severe injury while 0.02 ml causes severe injury.

Since any corneal injury caused is moderate in nature and reversible in Patty's and Grant's assessments of the results of the work of Carpenter and Smyth, a classification of 2 is concluded to be appropriate.

Skin - Classification: 2

Output statement numbers: 2, 17g, 7b, 17i

Exceptions: 20a deleted

Treon et al. report a "MLD for cutaneous application of undiluted cyclohexanone to the clipped uncovered skins of rabbits of doses equivalent to 10.2 - 23 g/kg." They continue, "symptoms were similar to those produced by cyclohexanol when applied on successive days . . . including local injury, central nervous system irritation (tremors and athetoid movements), hypothermia, local ulcers and a general thickening of the skin." Deichmann and Gerarde note, "five rabbits dosed with 1 ml on shaved intact skin showed no primary irritation." They add, "skin patch tests after the tenth day were negative." According to Union Carbide, "the undiluted chemical caused redness of short duration on the tender skin of the rabbit belly." Patty concludes, "an occasional skin contact with the liquid probably should cause no irritation." Prolonged or frequent skin contact "may logically be expected to result in irritation or dermatitis." He further notes that "absorption of toxic

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amounts are not likely to be a problem unless excessive exposures are encountered." Cyclohexanone is 15% soluble in water. It has a flash point of 111 degrees F and a vapor pressure of 2 mm Hg at 20 degrees C.

A classification of 2 is concluded to be appropriate to prevent repeated or prolonged contact which may result in the cited effects. The comments of Deichmann and Gerarde and Patty confirm the judgment that specification of statement 20a is not warranted for this substance

Ingestion: Classification: 0

Output statements: None

Exceptions: None

Union Carbide reports cyclohexanone to be "moderately hazardous" with an oral rat LD50 of 3.46 g/kg. Browning gives an oral rabbit MLD of 1600 - 1900 mg/kg. Thienes and Haley report "five male and five female rabbits survived 208 daily oral doses of 0.16 g/kg but growth, especially of males, was greatly retarded." Treon et al. report "following oral administration, animals exhibited paresis of the hind legs, narcosis deep and slow respiration, severe diarrhea and subsequent weight loss." They continue, "doses ranging from 1.0 - 1.9 g/kg were fatal to three rabbits in 18 minutes to 39 hours - 2 rabbits lost practically no weight because of short survival time but the other lost 135 g before death." They add, "following oral administration of cyclohexanone, the characteristics and sequence of symptoms are the same as given for cyclohexanol including ataxia, lethargy, collapse, narcosis and loss of reflexes." Patty gives a MLD for mice of 1.3 - 1.5 g/kg.

Since the substance is a liquid, is only moderately toxic, and was survived by the 10 rabbits given 208 daily oral doses of 0.16 g/kg, it is concluded that ingestion would not be a problem in the work place in the context of this standard.

RESPIRATOR TABLE DOCUMENTATION

NCE: Cyclohexanone

L. STANDARD: 50 ppm

PG PROPERTIES:

Odor Threshold: According to the Department of Transportation's "CHRIS Hazardous Chemical Data", the odor threshold of cyclohexanone is 0.12 ppm.

Eye Irritation Level: The AIHA Hygienic Guides reports that definite eye irritation occurs at 75 ppm cyclohexanone.

Other Information: The AIHA Hygienic Guides report that "Humans were exposed to various concentrations of cyclohexanone vapor for a period of 3 to 5 minutes. Twenty-five ppm was not objectionable to most subjects, but 50 ppm was uncomfortably irritating, particularly to the throat. Definite eye, nose and throat irritation was reported at 75 ppm."

Evaluation of Warning Properties: Through its odor and irritant effects, cyclohexanone can be detected at the permissible exposure limit. For the purposes of this standard, it is treated as a material with adequate warning properties. Gas sorbent respiratory equipment is permitted.

5000 ppm

Basis for IDLH Value: The AIHA Hygienic Guides report that "a 4-hour exposure of rats to 4000 ppm did not produce death but a concen-

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tration of 8000 ppm caused anesthesia and death." In addition, as described below, Patty reports that "typical narcotic symptoms have been observed in guinea pigs exposed for 6 hours to 4000 ppm cyclohexanone."

Other Toxicological Information: According to the AIHA Hygienic Guides, "breathing vapor constitutes the prime route of absorption by the body. The most important effects of inhalation of concentrations in excess of the Threshold Limit Value are irritation and narcosis."

The Hygienic Guides do not give an IDLH concentration but report that "a 4-hour exposure of rats to 4000 ppm did not produce death but a concentration of 8000 ppm caused anesthesia and death."

Patty reports that "Specht, Miller, Valaer, and Sayers observed that a 6-hour exposure of guinea pigs to 4000 ppm of cyclohexanone caused typical narcotic symptoms, lachrymation, salivation, depression of body temperature and respiratory heart rates, and opacity of the corneas. Recovery from the effects of narcosis was slow."

11,000 ppm at 212°F

PRESSURE AT 20 C: 2 mm Hg

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USE/EXPOSURE AND CONTROL DOCUMENT

CYCLOHEXANONE

Use/Exposure	Principal Route of Entry	Currently Used Control Methods
Inhalation of vapor and skin contact with liquid during synthesis of caprolactam nylon 6 production)	A,B	Local exhaust ventilation; personal protective equipment (protective clothing, goggles, chemical cartridge respirator)
Inhalation of vapor and skin contact with liquid during synthesis of adipic acid primarily nylon 66 and engineering plastics pro- duction)	A,B	Local exhaust ventilation; personal protective equipment (protective clothing, goggles, chemical cartridge respirator)
Inhalation of vapor and skin contact with liquid during synthesis and packaging of substance	A,B	Local exhaust ventilation; personal protective equipment (protective clothing, goggles, chemical cartridge respirator)
Inhalation of vapor and skin contact with liquid during surface coating operations primarily lacquers and vinyl solution coatings, spray painting of fabric and plastic textiles, and inks)	A,B	Local exhaust ventilation; personal protective equipment (protective clothing, goggles, chemical cartridge respirator)
Inhalation of vapor and skin contact with liquid during cleaning operations (leathers, textiles, and dry cleaning)	A,B	Local exhaust ventilation; personal protective equipment (protective clothing, goggles, chemical cartridge respirator)
Inhalation of vapor and skin contact with liquid during degreasing operations leathers, metals -- especially nickel sheets)	A,B	Local exhaust ventilation; personal protective equipment (protective clothing, goggles, chemical cartridge respirator)
Inhalation of vapor and skin contact with liquid during other operations involving use as solvent (crude rubber, insecticides, sludge solvent in aircraft lubrication oil, and epoxy resins)	A,B	Local exhaust ventilation; personal protective equipment (protective clothing, goggles, chemical cartridge respirator)

A -- Inhalation

B -- Skin contact resulting in

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- localized irritation
- C -- Ingestion
- D -- Skin contact resulting in
absorption and subsequent
systemic poisoning