OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR β -CHLOROPRENE

INTRODUCTION

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 Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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

SUBSTANCE IDENTIFICATION

Formula

C4H5Cl

Structure

H2C=CCICH=CH2

Synonyms

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

chloroprene

· Identifiers

1. CAS No.: 126-99-8

2. RTECS No.: EI9625000

3. DOT UN: 1991 30

4. DOT label: Flammable liquid

Appearance and odor

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

CHEMICAL AND PHYSICAL PROPERTIES

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

· Reactivity

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

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- 3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and hydrogen chloride) may be released in a fire involving β -chloroprene.
- 4. Special precautions: None reported

Flammability

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

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

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

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for β -chloroprene is 25 ppm (90 mg/m³) as an

8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for β -chloroprene is 1 ppm (3.6 mg/m³) as a ceiling limit [NIOSH 1992]. A worker's exposure to β -chloroprene shall at no time exceed this limit. However, β -chloroprene has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration.

ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned β -chloroprene a threshold limit value (TLV) of 10 ppm (36 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned β -chloroprene a "Skin" notation [ACGIH 1993].

· Rationale for limits

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

HEALTH HAZARD INFORMATION

· Routes of exposure

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

Summary of toxicology

Effects on Animals: β-Chloroprene causes eye, skin, and respiratory tract irritation, central nervous system depression, liver damage, and reproductive/developmental effects in experimental animals. Acutely poisoned animals showed inflammation of the eyes and mucous membranes and signs of central nervous system depression before dying of respiratory failure [Hathaway et al. 1991]. The oral LD₅₀ is 450 mg/kg in rats and 146 mg/kg in mice [NIOSH 1993]. The lowest lethal concentration in rats is 2,280 ppm for

- 4 hr [Sax and Lewis 1989]. Rats exposed 6 hr/day, 5 days/week for 4 weeks to a β -chloroprene concentration of 40 ppm showed signs of eye and skin irritation and growth depression; when the concentration was increased to 160 or 625 ppm, the animals showed loss of hair, signs of liver damage, and an increased rate of mortality [Hathaway et al. 1991]. By inhalation, chloroprene caused sterility or impotence in more than 50% of rats and mice exposed for 8 hr to concentrations ranging from 120 to 6,227 ppm (rats) or 12 to 152 ppm (mice) [ACGIH 1991; Hathaway et al. 1991]. Studies of chloroprene's embryotoxicity and teratogenicity have reported conflicting results [ACGIH 1991]. The International Agency for Research on Cancer (IARC) concluded that there was inadequate evidence in experimental animals to classify β -chloroprene's carcinogenicity [IARC 1987].
- 2. Effects on Humans: β-Chloroprene causes eye and skin irritation as well as central nervous system depression and may have reproductive, mutagenic, embryotoxic, and/or carcinogenic effects. In contact with the eyes or skin, chloroprene can cause chemical burns [Hathaway et al. 1991]. One fatality involving a worker exposed for 3 to 4 min to an unspecified chloroprene concentration in an unventilated vessel has been reported [ACGIH 1991; Hathaway et al. 1991]. Exposure to β -chloroprene concentrations ranging from 56 to greater than 334 ppm for a 1-month period was associated with hair loss, personality changes, irritability, extreme fatigue, and unbearable chest pain [Hathaway et al. 1991]. Volunteers exposed to a 973-ppm concentration of chloroprene for 15 min experienced nausea and giddiness; when these subjects performed light exercise during the exposure, they experienced these symptoms within 10 min [ACGIH 1991; Hathaway et al. 1991]. Studies of workers exposed to this substance at concentrations of 5 ppm or less report a significant increase in chromosome aberrations, and reproductive effects have been seen in male workers exposed to 0.28 to 1.94 ppm concentrations of chloroprene [Hathaway et al. 1991]. The wives of these workers also reportedly experienced a threefold excess of miscarriages [Hathaway et al. 1991]. Epidemiological studies of chloroprene-exposed workers have yielded conflicting results in the past; however, a recent study of maintenance workers showed a dose-related increase in the incidence of liver, lung, and lymphatic cancers among these workers [Hathaway et al. 1991].

Signs and symptoms of exposure

- Acute exposure: Acute exposure to β-chloroprene may cause redness and inflammation of the eyes and eyelids, corneal necrosis, skin burns, nausea, dizziness, giddiness, personality changes, headache, irritability, reversible hair loss, insomnia, extreme fatigue, respiratory irritation, and severe chest pains.
- Chronic exposure: Chronic exposure to β-chloroprene may cause effects on spermatogenesis or sperm morphology; increased risk of miscarriage; chromosome aberrations; and cancer of the lung, liver, and lymphatic system.

Emergency procedures

WARNING!

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

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

- 1. Eye exposure: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of β -chloroprene! Immediately but gently flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.
- 2. Skin exposure: Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! Immediately, continuously, and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.
- 3. Inhalation exposure: Move the victim to fresh air immediately.

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

- 4. Ingestion exposure: Take the following steps if β -chloroprene or any material containing it is ingested:
 - -Do not induce vomiting.
 - —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and no more.
 - —Do not permit the victim to drink milk or carbonated beverages!
 - —Do not permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

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

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

EXPOSURE SOURCES AND CONTROL METHODS

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

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

- -Process enclosure
- -Local exhaust ventilation
- -General dilution ventilation
- -Personal protective equipment

Good sources of information about control methods are as follows:

- ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
- Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
- 5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

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

• Preplacement medical evaluation

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

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

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

Periodic medical examinations and biological monitoring

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

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

Medical examinations recommended at the time of job transfer or termination

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

WORKPLACE MONITORING AND MEASUREMENT

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

PERSONAL HYGIENE

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

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

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

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

STORAGE

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

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

SPILLS AND LEAKS

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

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

SPECIAL REQUIREMENTS

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

• Emergency planning requirements

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

Reportable quantity requirements for hazardous releases

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

· Community right-to-know requirements

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

· Hazardous waste management requirements

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

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

RESPIRATORY PROTECTION

· Conditions for respirator use

Good industrial hygiene practice requires that engineer-

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

• Respiratory protection program

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

PERSONAL PROTECTIVE EQUIPMENT

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

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

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

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