OCCUPATIONAL SAFETY AND GUIDELINE FOR CYCLOHEXYLAMINE

INTRODUCTION

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 Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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

SUBSTANCE IDENTIFICATION

Formula

 $C_6H_{11}NH_2$

Structure



Synonyms

Aminocyclohexane, aminohexahydrobenzene, CHA, cyclohexanamine, hexahydroaniline, hexahydrobenzenamine

Identifiers

1. CAS No.: 108-91-8

2. RTECS No.: GX0700000

3. DOT UN: 2357 68

4. DOT label: Flammable liquid; corrosive

Appearance and odor

Cyclohexylamine is a flammable, colorless or yellow liquid with a strong, fishy, amine odor. The odor threshold of cyclohexylamine is 2.6 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

· Physical data

1. Molecular weight: 99.17

2. Boiling point (760 mm Hg): 134.5°C (274.1°F)

3. Specific gravity (water = 1): 0.87 at $25^{\circ}C$ ($77^{\circ}F$)

4. Vapor density (air = 1 at boiling point of cyclohexy-lamine): 3.42

5. Melting point: -17.7°C (0.14°F)

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- 6. Vapor pressure at 20°C (68°F): 11.3 mm Hg
- Solubility: Completely soluble in water and most organic solvents, including alcohols, ethers, ketones, esters, and chlorinated hydrocarbons; also soluble in peanut oil, mineral oil, acetone, and benzene.
- 8. Evaporation rate (ether = 1): 82.9

Reactivity

- Conditions contributing to instability: Heat, sparks, and open flame. Contact of the vapor with air generates an explosive mixture.
- Incompatibilities: Contact of cyclohexylamine with oxidizers, organic compounds, acid anhydrides, acid chlorides, alkylene oxides, acids, any copper alloy, zinc, or galvanized steel may cause a violent reaction.
- Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving cyclohexylamine.
- Special precautions: Avoid contact of the vapors with air.

- Flammability

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

- 1. Flash point: 31°C (88°F) (open cup)
- 2. Autoignition temperature: 293°C (560°F)
- 3. Flammable limits in air (% by volume): Lower 1.5; upper 9.4
- 4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to fight fires involving cyclohexylamine. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

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

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclohexylamine [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (40 mg/m³) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

ACGIH TLY

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclohexylamine a threshold limit value (TLV) of 10 ppm (41 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

· Rationale for limits

The NIOSH and ACGIH limits are based on the risk of severe eye and skin irritation associated with exposure to cyclohexylamine.

HEALTH HAZARD INFORMATION

· Routes of exposure

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

Summary of toxicology

1. Effects on Animals: Cyclohexylamine is a severe irritant of the eyes, mucous membranes, and skin in animals. A single drop of a 50% aqueous solution of cyclohexylamine onto the conjunctival sac of a rabbit's eye caused complete destruction of the eye [ACGIH 1991]. When applied to the skin of rabbits, this substance caused severe skin damage [NIOSH 1990]. Although skin sensitization tests in guinea pigs yielded negative results, cyclohexylamine is believed to have weak sensitizing potential [ACGIH 1991; NJDH 1991]. The dermal LD₅₀ in rabbits is 277 mg/kg [NIOSH 1990]. Fifty percent of exposed rats died after inhaling a cyclohexylamine concentration of 7,500 mg/m³ for an unspecified time [NIOSH 1990]. Acutely poisoned animals displayed signs of severe irritation and of central nervous system effects before death [NIOSH 1990]. Rabbits, rats, and guinea pigs exposed for 7 hr/day, 5 days/week to a 1,200ppm concentration of cyclohexylamine died after a single exposure; however, most animals exposed to a 150-ppm concentration on the same regimen survived for 10 such exposures. Before death, animals of all species exhibited signs of eye and respiratory tract irritation and developed corneal opacities [Clayton and Clayton 1981]. The oral LD₅₀ is 156 mg/kg for rats and 224 mg/kg for mice [NIOSH 1990]. In rats, cyclohexylamine has caused reproductive effects in males (reduction in the number and size of litters sired) and females (reduction in pregnancy rate, number of live-born fetuses and post-natal survivors, and birthweight of offspring) [Clayton and Clayton 1981]. In experiments involving rats, mice, and dogs, cyclohexylamine has induced fetotoxic and/or paternal reproductive effects by oral, intraperitoneal, and parenteral administration INIOSH 19901. Cyclohexylamine has caused chromosomal breaks in a number of in-vitro test systems [IARC 1980]. Cyclohexylamine has been tested for carcinogenicity in two oral bioassays in mice and four in rats. Based on the results of this research, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of cyclohexylamine in animals is inadequate [IARC 1980].

2. Effects on Humans: Cyclohexylamine is a severe irritant of the eyes, skin, mucous membranes, and respiratory tract in humans; it may also cause skin sensitization in some individuals. Cyclohexylamine has caused severe irritation upon contact with the skin; patch tests have shown that this substance is capable of causing skin sensitization [NIOSH 1990; Clayton and Clayton 1981]. Three workers who had been accidentally overexposed to an unspecified concentration of cyclohexylamine experienced symptoms of lightheadedness, drowsiness, anxiety, apprehension, and nausea; one acutely poisoned worker also developed slurred speech and vomited [Hathaway et al. 1991]. Human volunteers who ingested 5 grams of cyclohexylamine a day for 7 or 8 consecutive days showed no adverse effects; workers exposed to airborne concentrations of this substance in the range of 4 to 10 ppm also reported experiencing no symptoms [ACGIH 1991].

· Signs and symptoms of exposure

- Acute exposure: Acute exposure to cyclohexylamine can cause severe irritation of the eyes, with tearing and conjunctivitis; irritation of the respiratory tract, with coughing and difficult breathing; and severe skin irritation, with burns, blisters, redness, swelling, and cell death. Acutely poisoned workers also may experience apprehension, drowsiness, lightheadedness, and vomiting.
- Chronic exposure: Repeated or chronic exposure to cyclohexylamine may cause corneal opacities, dryness and cracking of the skin, and, in some individuals, skin sensitization, with itching, wheals, and redness of the affected areas.

Emergency procedures

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

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

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

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

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

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

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

EXPOSURE SOURCES AND CONTROL METHODS

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

- —Use as an intermediate in the production of cyclamate sweeteners and textile and rubber chemicals
- —Use as a corrosion inhibitor in boiler feed water and oil fields and in the packaging of metal equipment
- —Manufacture of dyes, insecticides, plasticizers, emulsifying agents, acid gas absorbents, and dry-cleaning soaps

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

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

Good sources of information about control methods are as follows:

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

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveil-

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

Preplacement medical evaluation

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

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

Periodic medical examinations and biological monitoring

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

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

Medical examinations recommended at the time of job transfer or termination

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

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyclohexylamine is determined by using a silica gel tube (600/150/150-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 96 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in Method P&CAM 221 of the NIOSH Manual of Analytical Methods [NIOSH 1977].

PERSONAL HYGIENE

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

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

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

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

STORAGE

Cyclohexylamine should be stored in a cool, dry, wellventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of cyclohexylamine should be protected from physical damage and should be stored separately from strong oxidizers (such as chlorine, bromine, and fluorine), acids, copper alloys, lead, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle cyclohexylamine. To prevent static sparks, containers and equipment should be grounded and bonded for transfers. Because containers that formerly contained cyclohexylamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

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

- 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.

- Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
- For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
- For large liquid spills, build dikes far ahead of the spill to contain the cyclohexylamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

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

• Emergency planning requirements

Employers owning or operating a facility at which there are 10,000 lb or more of cyclohexylamine must comply with EPA's emergency planning requirements [40 CFR Part 355.30].

Reportable quantity requirements for hazardous releases

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

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

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

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

· Community right-to-know requirements

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

Hazardous waste management requirements

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

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

RESPIRATORY PROTECTION

· Conditions for respirator use

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

Respiratory protection program

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

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, or gauntlets, as appropriate) should be worn to prevent any skin contact with cyclohexylamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have breakthrough times of less than 1 hr and are not recommended for use with cyclohexylamine: butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl alcohol, polyvinyl chloride, and Viton.

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

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

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