OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLIC ACID

INTRODUCTION

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 Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information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

SUBSTANCE IDENTIFICATION

• Formula

 $C_3H_4O_2$

Structure

 $CH_2 = CHCO_2H$

Synonyms

Propenoic acid, acroleic acid, ethylenecarboxylic acid, propene acid, vinylformic acid, glacial acrylic acid, 2-propenoic acid

• Identifiers

1. CAS No.: 79-10-7

2. RTECS No.: AS4375000

DOT UN: 2218 29
 DOT label: Corrosive

Appearance and odor

Acrylic acid is a colorless, corrosive, combustible liquid with a distinctive and acrid odor. The odor threshold is reported to be 1.0 part per million (ppm) parts of air. Acrylic acid is available commercially in the United States in two forms: the technical grade (which contains 94% acrylic acid) and glacial acrylic acid (which contains 98% acrylic acid).

CHEMICAL AND PHYSICAL PROPERTIES

Physical data

- 1. Molecular weight: 72.1
- 2. Boiling point (760 mm Hg): 141°C (221.8°F)
- 3. Specific gravity (water = 1): 1.06 at 20°C (68°F)
- 4. Vapor density (air = 1 at boiling point of acrylic acid): 2.5
- 5. Melting point: 14°C (57.2°F)
- Vapor pressure at 20°C (68°F): 3.1 mm Hg
- 7. Solubility: Miscible with water, alcohol, ether, acetone, and benzene
- 8. Evaporation rate (butyl acetate = 1): Greater than 1

• Reactivity

- 1. Conditions contributing to instability: The vapor forms an explosive mixture in contact with the air. Heat, sparks, open flame, oxygen, high temperature, and pressure.
- 2. Incompatibilities: Fires and explosion may result from contact of acrylic acid with oxydizing agents, amines, alkalis, ammonium hydroxide, chlorosulfonic acid, ethylene diamine, ethyleneimine, oleum, or 2-aminoethanol.
- 3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released in a fire involving acrylic acid.
- 4. Special precautions: Acrylic acid corrodes carbon steel and other metals.

• Flammability

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

- 1. Flash point: 50°C (122°F) (open cup)
- 2. Autoignition temperature: 438°C (820°F)
- 3. Flammable limits in air (% by volume): Lower, 2.4; upper, 8.0
- 4. Extinguishant: Use dry chemical, water spray, alcohol foam, or carbon dioxide to fight fires involving acrylic acid.

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Water may be ineffective, but it may be used to cool fireexposed 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 acrylic acid should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. 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 acrylic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. 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 (including a self-contained breathing apparatus) when fighting fires involving acrylic acid. Firefighters' protective clothing may not provide protection against permeation by acrylic acid.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylic acid is 10 ppm (30 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-Al.

• NIOSH REL

The National Institute for Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (6 mg/m³) as an 8-hr TWA with a "Skin" notation [NIOSH 1988, 1992].

ACGIH TLV[®]

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acrylic acid a threshold limit value (TLV) of 2 ppm (5.9 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991]. The ACGIH TLV also bears a "Skin" notation.

• Rationale for limits

The OSHA limit was established to protect workers from the risk of eye and nasal irritation. The NIOSH and ACGIH limits were based on recent studies demonstrating degeneration of nasal mucosa at 5 ppm, changes in pulmonary function, teratogenicity and embryotoxicity in rats at low doses, and skin absorption in animals.

HEALTH HAZARD INFORMATION

• Routes of exposure

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

Summary of toxicology

1. Effects on Animals: Acrylic acid is dermally absorbed and is corrosive to the eyes, nose, and mucous membranes in animals. Application of glacial acrylic acid to the eyes of rabbits caused irreversible corneal injury graded 9 on an ascending severity scale of 1 to 10 [Grant 1986]. Application of a 1% solution to the eye of a rabbit caused severe burns and eye injury [ACGIH 1991a; NIOSH 1991; Proctor et al. 1988]. Irreversible eye and skin damage resulted following exposure of rats to 1,200 ppm for 4 hr [NLM 1992]. Applied to rabbit skin, acrylic acid caused severe irritation [Proctor et al. 1988]. Three of five guinea pigs became dermally sensitized when exposed to acrylic acid by injection and subsequently challenged with this substance [Clayton and Clayton 1981]. The dermal LD50 in rabbits is 290 mg/kg [NLM 1992]. Saturated atmospheres have been reported to range from 420 ppm at 20° to 760 ppm at 30° [NLM 1992]. Although exposure of rats to polymerized saturated vapors (room temperature) for 8 hr did not induce deaths [Smyth et al. 1962], a 1-hr exposure to unpolymerized saturated vapor was the maximum duration tolerated without death [Carpenter et al. 1974]. Vapor concentrations approaching saturation killed half of a group of rats exposed for 3.5 hr [NLM 1992]. However, 4-hr exposures of rats at 2,000 or 4,000 ppm were nonlethal [NLM 1992; Carpenter et al. 1974]. The 4-hr LC₅₀ in rats is 1,200 ppm [NLM 1992]. Exposure of rats to irritant concentrations of acrylic acid caused decreased respiratory rates and tidal and minute volumes [ACGIH 1991a]. In addition, four rats exposed once to 6,333 ppm of acrylic acid for 5 hr developed eye and nose irritation, respiratory difficulties, and unresponsivness; one animal died. At autopsy, these animals showed lung, liver, and kidney damage [ACGIH 1991a]. The oral LD50 in rats was variable: 357, 1,250, or 2,722 mg/kg [NLM 1992; Smyth et al. 1962]. Rats exposed to acrylic acid at 80 ppm for 6 hr/day, 5 days/week for 4 weeks showed no adverse effects, and rats exposed to 300 ppm on the same regimen experienced nose irritation, lethargy, and decreased weight

- gain. Rats exposed to 1,500 ppm acrylic acid for shorter intervals showed damage to the liver, kidneys, and lungs at autopsy [ACGIH 1991a]. However, rats that inhaled 233 ppm for 4 hr/day, 5 days/week for 4 weeks developed gastric mucosal lesions and pulmonary inflammation [NLM 1992]. In rats exposed to the vapors of acrylic acid at 5, 25, or 75 ppm for 6 hr/day, 5 days/week for 13 weeks, terminal pathology was normal in the 5- or 25-ppm group; however, slight degenerative lesions of the olfactory mucosa were present in the high-dose group [ACGIH 1991a]. Similarly exposed mice were more sensitive than rats as they developed lesions of the nasal mucosa for all three exposure concentrations [ACGIH 1991a]. Intraperitoneal or intraamniotic injections of acrylic acid caused embryotoxicity and gross abnormalities in the offspring of treated pregnant rats [Proctor et al. 1988; NLM 1992].
- 2. Effects on Humans: Acrylic acid is corrosive on contact with the eyes, skin, mucous membranes, and upper respiratory tract of humans, and its vapor causes severe irritation of these organs. Acute industrial exposure to this substance has caused eye and skin burns ranging in intensity from moderate to severe [Proctor et al. 1988]. Absorption of acrylic acid through the skin has been reported to cause systemic illness, and inhalation of the mist or vapor of acrylic acid may cause lung injury as well as nasal irritation and tearing of the eyes [Genium 1989]. Based on effects seen in animals, acrylic acid may cause skin sensitization [ACGIH 1991a].

Signs and symptoms of exposure

- 1. Acute exposure: Acute exposure to acrylic acid can cause redness, swelling, and tearing of the eyes, runny nose, scratchy throat, coughing, and difficult breathing. Contact of the liquid with the eyes or skin can cause corneal injury, irritation, burns, and destruction of the tissue.
- 2. Chronic exposure: Chronic exposure to acrylic acid may cause lethargy, irritation, and skin sensitization reactions.

• Emergency procedures



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 acrylic acid. Immediately but gently flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.
- 2. Skin exposure: Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove contaminated clothing! Immediately, continuously, and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.
- 3. Inhalation exposure: If vapors, mists, or aerosols of acrylic acid are inhaled, move the victim to fresh air immediately.

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

- 4. Ingestion exposure: Take the following steps if acrylic acid or a solution containing it is ingested:
- -Seek medical attention immediately.
- —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.

1992

EXPOSURE SOURCES AND CONTROL METHODS

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

- -Manufacture of acrylic resins, especially the acrylates
- Use of acrylic acid in acrylic polymeric emulsions for leather, textile, and paper coatings
- Use of acrylic acid in paints, floor polishes, adhesives, general finishes, and binders
- Manufacture of plastics, molding powder for signs, construction units, decorative emblems, and insignia
- -Use of acrylic acid in dentistry and medicine

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

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

Good sources of information about control methods are as follows:

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

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, 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 acrylic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

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

Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrylic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying

the adverse effects of acrylic acid on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

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

Medical examinations recommended at the time of job transfer or termination

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

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acrylic acid is determined by using two XAD-8 tubes connected in series. Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 24 liters is collected. The sample is then treated with methanol and water (1:1) to extract the acrylic acid. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method has a sampling and analytical error of 0.12 and is found in OSHA Method No. 28, OSHA Analytical Methods Manual [OSHA 1985].

PERSONAL HYGIENE

If acrylic acid contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, followed by washing with soap and water.

Clothing contaminated with acrylic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrylic acid, particularly its potential to cause skin burns.

A worker who handles acrylic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities. Workers should not eat, drink, or use tobacco products in areas where acrylic acid or a solution containing acrylic acid is handled, processed, or stored.

STORAGE

Acrylic acid is explosive unless (1) an inhibitor has been added to it before it is stored, or (2) it is stored at temperatures below its melting point. Acrylic acid should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; the storage area must meet the requirements for an OSHA Class II combustible liquid. Explosionproof exhaust ventilation and sparkproof fans must be used in storage areas. Storage tanks should be made of stainless steel or aluminum. Containers of acrylic acid should be protected from physical damage and should be stored separately from oxidizers, amines, alkalies, other incompatible substances, heat, sparks, and open flame. Only nonsparking tools may be used to handle acrylic acid. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained acrylic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

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

- 1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
- 2. Notify safety personnel.
- 3. Remove all sources of heat and ignition.
- 4. Ventilate potentially explosive atmospheres.
- 5. Use water spray to reduce vapors, but the spray may not prevent ignition in closed spaces.
- 6. Use nonsparking tools for cleanup.
- 7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
- 8. For large liquid spills, build dikes far ahead of the spill to contain the acrylic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

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

• Emergency planning requirements

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

Reportable quantity requirements for hazardous releases

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulation resulting from 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 acrylic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

- —Notify the National Response Center *immediately* at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].
- —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].
- —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

• Community right-to-know requirements

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acrylic acid per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release

Inventory Form (Form R) to EPA reporting the amount of acrylic acid emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acrylic acid is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U008. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acrylic acid may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

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

RESPIRATORY PROTECTION

Conditions for respirator use

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

Respiratory protection program

Employers should institute a complete respiratory 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, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the NIOSH Respirator Decision Logic [NIOSH 1987b] and the NIOSH Guide to Industrial Respiratory Protection [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any possibility of skin contact with acrylic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acrylic acid and have demonstrated good-to-excellent resistance for periods greater than 8 hr: butyl rubber and Saranex. Materials that may withstand permeation for more than 4 hr but fewer than 8 hr: Teflon and Viton. Natural rubber, neoprene, nitrile rubber, polyethylene, and polyvinyl chloride have demonstrated poor resistance to permeation by acrylic acid.

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

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

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