POLLUTION CONTROL AND SAFETY

Acrylic acid is a colourless liquid with an irritating acrid odour at room temperature and pressure. Its odour threshold is low $(0.20-3.14 \text{ mg/m}^3)$. It is miscible in water and most organic solvents.

Acrylic acid polymerizes easily when exposed to heat, light or metals, and so a polymerization inhibitor is added to commercial acrylic acid to prevent the strong exothermic polymerization. The inhibitors that are usually used in acrylic acid preparations are the

- monomethyl ether of hydroquinone (methoxyphenol) at 200 ± 20 ppm
- phenothiazine at 0.1%
- hydroquinone at 0.1%.
- Methylene blue at 0.5 to 1.0%
- N,N'-diphenyl- p-phenylenediamine at 0.05%

The presence of oxygen is required for the stabilizer to function effectively. A head space containing sufficient air should always be maintained above the monomer to ensure inhibitor effectiveness. Dissolved oxygen takes part in the inhibition reaction and therefore is gradually consumed. The level of dissolved oxygen should periodically be replenished. This can be accomplished by thoroughly aerating the liquid phase, i.e. recirculation of the inventory in tanks or agitating drums (rotating).

Acrylic acid must never be handled under an inert atmosphere.

Freezing of acrylic acid occurs at 13°C. Rethawing under inappropriate temperature conditions is another frequent reason for acrylic acid polymerization. During the crystallization process the inhibitor and oxygen concentrate in the mother liquor. Therefore no mother liquor should be withdrawn from a partially frozen container. This may result in a severe deficiency of the inhibitor system in the crystalline matrix. If direct heat is applied, polymerization will start immediately, often with great violence. Under no circumstances must steam be used to thaw frozen acrylic acid, nor must thawing be carried out at temperatures above 35°C.

Acrylic acid is a strong corrosive agent to many metals, such as unalloyed steel, copper and brass. Frequently the hydrolysis of such metalic materials generates a deep discoloration in acrylic acid. Polyvalent metal salts formed during hydrolytic reactions could also induce polymerization. Therefore, under no circumstances should acrylic acid be stored or transported with equipment which contains the above-mentioned metals. Acrylic acid does not affect stainless steel.

Analytical Methods

Acrylic acid residues in air and other media can be quantified by means of gas chromatographic, high performance liquid chromatographiC was found to be 14 mg/m³ (14 ppm) in air and down to 1 mg/kg or 1 mg/litre (1 ppm) in other media.

Human Exposure

No data on general population exposure are available. However, consumers may be exposed to unreacted acrylic acid in household goods such as polishes, paints and coatings, adhesives, rug backing, plastics, textiles and paper finishes. A potential source of internal exposure to acrylic acid may result from metabolism of absorbed acrylic acid esters. Acrylic acid also occurs in wastewater effluent from its production. It is estimated that thousands of workers could be exposed to acrylic acid, but exact figures are not available.

Kinetics and Metabolism

Inhalation and contact with skin are important routes of occupational exposure. Regardless of the route of exposure, acrylic acid is rapidly absorbed and metabolized. It is extensively metabolized, mainly to 3-hydroxypropionic acid, CO_2 and mercapturic acid, which are eliminated in the expired air and urine. Owing to its rapid metabolism and elimination, the half-life of acrylic acid is short (minutes) and therefore it has no potential for bioaccumulation.

Effects on Animals

Most data indicate that acrylic acid is of low to moderate acute toxicity by the oral route, and of moderate acute toxicity by the inhalation and dermal routes.

Acrylic acid is corrosive or irritant to skin and eyes. It is unclear what concentration is non-irritant. It is also a strong irritant to the respiratory tract.

A chronic drinking-water study on rats showed no effect at the highest dose tested (78 mg/kg body weight per day). For inhalation studies a lowest-observed- adverse-effect level (LOAEL) of 15 mg/m³ (5 ppm) was observed in mice exposed to acrylic acid for 90 days.

Available data do not provide evidence for an indication of carcinogenicity of acrylic acid, but the data are inadequate to conclude that no carcinogenic hazard exist.

Effects on Humans

There have been no reports of poisoning incidents in the general population. No occupational epidemiological studies have been reported.

Because acrylic acid toxicity occurs at the site of contact, separate guidance values are recommended for oral and inhalation exposure. Guidance values of 9.9 mg/litre for drinking-water and $54 \mu g/m^3$ for ambient air for the general population are proposed.

Effects of the Environment

No quantitative data on environmental levels of acrylic acid in ambient air, drinking-water or soil have been reported.

Acrylic acid is miscible with water and, therefore, would not be expected to adsorb significantly to soil or sediment. Under soil conditions, chemicals with low Henry's Law constants are essentially non-volatile. However, the vapour pressure of acrylic acid would suggest that it may volatilize from surfaces and dry soil. Acrylic acid may be formed by hydrolysis of acrylamide monomer from industrial waste in soil, especially under aerobic conditions. The toxicity of acrylic acid to bacteria and soil microorganisms is low.

Acrylic acid emitted into the atmosphere will react with photochemically produced hydroxyl radicals and ozone, resulting in rapid degradation. There is no potential for long-range atmospheric transport of acrylic acid because it has an atmospheric lifetime of less than one month.

When released into water, acrylic acid readily biodegrades. The fate of acrylic acid in water depends on chemical and microbial degradation. When added to water acrylic acid is rapidly oxidized, and so it can potentially deplete oxygen if discharged in large quantities into a body of water. Acrylic acid has been shown to be degraded under both aerobic and anaerobic conditions.

On the basis of the low octanol-water partition coefficient of acrylic acid, bioconcentration in aquatic organisms is unlikely. There have been no reports of biomagnification of acrylic acid in food chains.

Symptoms of poisoning

The principal hazard of acrylic acid is its corrosive effect on tissues. Both vapour and liquid can be irritating or corrosive to the mucous membranes, skin and eyes. The severity of these effects is dependent on the duration of contact, which, if prolonged, may result in blisters and burns. Blister formation can appear as late as 24 h after exposure. Severe corneal burns could occur to the eyes. Permanent tissue damage may result if prompt and appropriate emergency response is not provided.

Inhalation of concentrated vapours and mist could produce moderate to severe irritation of the respiratory tract. High concentrations could result in pulmonary oedema while lower concentrations could produce nasal and throat irritation. Lacrymation may also result from inhalation exposure.

Although ingestion is not an expected route of human exposure, swallowing of acrylic acid may cause severe irritation or burning of the mouth, throat, oesophagus or stomach.

No serious health effects have been reported to result from single exposure or repeated exposure at low concentrations of acrylic acid.

Safety in Use

Acrylic acid should only be handled in well-aerated and well-ventilated places. If exposure to concentrated vapour can not be excluded (as in the case of an accident), selfcontained breathing apparatus or air supply masks must be worn. Care must be taken when using filter-type masks to ensure that the filter capacity is not exceeded for the intended time of use and expected concentration.

In areas where a release of acrylic acid is possible, eye protection devices, face shields, neoprene gloves and rubber boots should be worn. A chemical suit with a self-

contained breathing apparatus is strongly recommended if larger spills or emissions have to be cleared. Appropriate protective clothing should be worn for work involving breaking or entering into a closed acrylic acid system. Owing to its vapour pressure, the concentration of acrylic acid in closed rooms can reach high values.

If clothing or shoes have accidentally been contaminated with acrylic acid, they must be removed immediately. Contaminated leather shoes or other leather goods must be discarded.

For timely and appropriate emergency response, it is advisable to provide complete sets of safety protection equipment near places where accidents with acrylic acid are possible.

Explosion and Fire Hazards

Acrylic acid has a flash point of 54-68°C and does not form explosible vapour mixtures at ordinary ambient temperatures. However, ignition may occur if excessive amounts of mist or aerosols have formed in air. Ignition sources can include spark discharges from static electricity, and this can occur when acrylic acid is flowing through or being discharged from a line. During transfer from one container into another, the containers should be electrically interconnected and properly grounded. Splashing into a tank should be avoided by using a dip tube.

Since acrylic acid and water are miscible in any proportion, water can be used to extinguish fires. Small fires can be fought with carbon dioxide or dry chemical extinguishers, whereas for larger fires foam (alcohol or universal type) can be used.

If a fire occurs in or close to a tank farm containing acrylic acid, tanks and pipes should be cooled by spraying with water in order to prevent the acid from polymerizing.

Storage

Acrylic acid should be stored in a detached, cool, well-ventilated, non-combustible place and its containers should be protected against physical damage. Acrylic acid can be stored only in vessels lined with glass, stainless steel, aluminum or polyethylene. In order to inhibit polymerization during transport and storage, 200 ppm MeHQ (the monomethyl ether of hydroquinone) is commonly added to acrylic acid by the manufacturer. The presence of oxygen is required for the inhibitor to be effective. A major concern during the storage of acrylic acid is the avoidance of elevated temperatures as well as freezing, since both can lead to a failure of the inhibitor system. Ideally acrylic acid should be stored within a temperature range of 15 to 25°C.

Acrylic acid and its solutions should be kept out of reach of children and unauthorized persons as well as away from food, drink and animal feed. If any container in the store is leaking, appropriate precautions should be taken (see section 6) and personal protective equipment used.

Transport

Acrylic acid is shipped in containers in compliance with regulations according to ADR/RID/GGVS/GGVE, Class 8 Packing Group B specifications. Acrylic acid is commonly shipped in steel drums with polyethylene inserts or in self-supporting high-density polyethylene drums impermeable to ultraviolet light. White polyethylene container are translucent to ultraviolet light and therefore may promote polymerization. Stainless steel ISO containers are recommended for the transport of quantities of acrylic acid up to 1 tonne.

Spillage

Before dealing with any spillage, appropriate personal protective equipment should be used . Small spills of up to 5 litres can be absorbed in commercially available clean-up kits (using sand or clay). If a wastewater sewer is close by, the spill can also be washed down with water provided that it is not a storm-sewer or ditch that is routed to surface water.

Large spills should be contained, if possible, within a dike area. A temporary dike can be arranged by stacking sand bags or similar devices. Avoid run-off into storm sewers routed to public surface water. If possible, the material should be recovered in appropriate containers for reuse or disposal. If a wastewater sewer is available, the acid or remainders can also be sparingly washed down after dilution and neutralization prior to being discharged to a water-treatment plant. During all handling operations of large spills a chemical suit with a self-contained or air-supplied breathing device must be worn.

In the event of accidental spillage of acrylic acid to surface water or to a municipal sewer system, the pollution control agencies must be notified promptly.

Spills of the monomer may be diluted and washed into a biological treatment plant. The biodegradability of the material in diluted form is good .However, acrylic acid may be toxic to the system if the bacteria have not been conditioned properly to this material. Accordingly, the initial feed rate should be low with a stepwise increase if a significant amount is to be fed into the biological treatment plant. The maximum concentration should not exceed 1000 mg per litre. It should be kept in mind, however, that large quantities may affect the optimal acidity of the milieu and may therefore need to be neutralized by the simultaneous addition of sodium hydroxide.

Disposal

Acrylic acid is a highly corrosive material. Accordingly it should always be handled with appropriate safety equipment. Solid materials containing acrylic acid, such as absorbents or polymeric material, can be disposed of by incineration. Disposal in landfills must be thoroughly checked with the authorities and should be practiced only as a last resort.

For the disposal of waste materials originating from laboratory samples, great care must be taken to keep the monomer separated from incompatible material, such as peroxides, which may initiate polymerization.

Specific Restrictions

In the USA acrylic acid as a commercial chemical product is classified as a toxic waste subject to regulation and notification requirements.

In the European Economic Community preparations that contain acrylic acid at concentrations greater than 25% should be considered as corrosive and at concentrations of 2-25% as irritant. Member States should ensure that dangerous preparations containing acrylic acid are not placed on the market unless their packages, fastenings and labels comply with requirements laid down.

In Canada, the maximum amount of acrylic acid that may be transported on a passenger aircraft, train or road vehicle is one litre. The maximum amount that may be transported on a cargo aircraft is 30 litres.