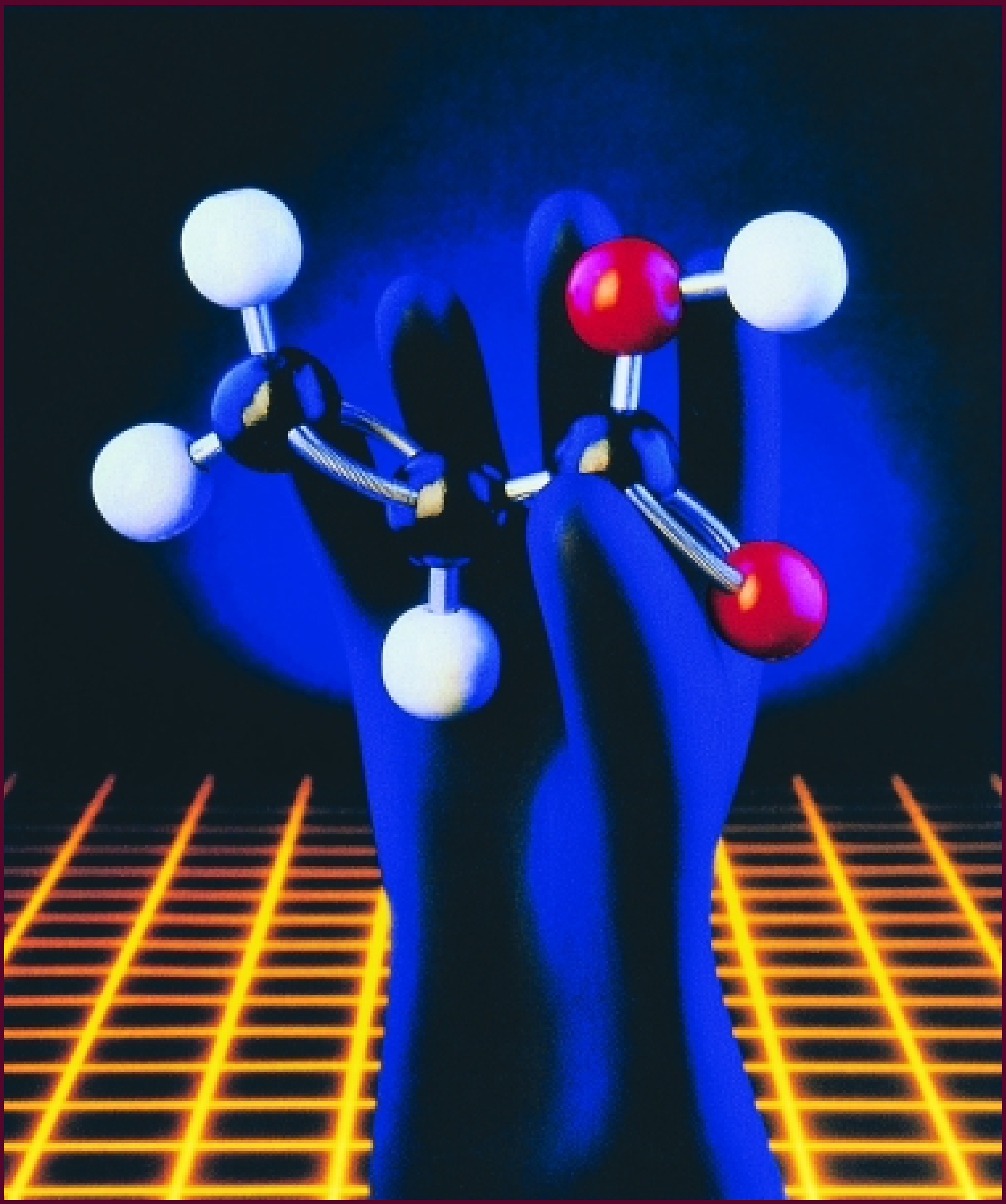
ACRYLIC ACID

A SUMMARY OF SAFETY AND HANDLING

3RD EDITION



Compiled by
BASF Corporation
Celanese, Ltd.
Elf Atochem North America, Inc.
Rohm & Haas Company
Union Carbide Corporation

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1 INTRODUCTION

The Intercompany Committee for the Safety and Handling of Acrylic Monomers, ICSHAM, consists of companies who are involved in manufacturing and/or marketing of acrylic acid and its basic esters (methyl, ethyl, butyl, and 2-ethylhexyl acrylate) in the United States of America. The group is committed to sharing information on the safe handling and storage of acrylic monomers among themselves, with their customers, carriers and other handlers of acrylic monomers. The member companies are, BASF Corporation, Celanese Ltd, Elf Atochem North America Inc, Rohm & Haas Company and Union Carbide Corporation.

The purpose of this brochure is to provide general information on the safe handling and storage of hydroquinone monomethyl ether (MEHQ) inhibited acrylic acid, hereafter referred to as acrylic acid. The information in this brochure, is based on research and experience by ICSHAM member companies in addition to information taken from accompanied references. It is suggested that this entire document along with your material safety data sheet (MSDS) be read before using the information provided. In addition you are strongly encouraged to call your acrylic acid supplier with any further questions you may have.

Acrylic acid will readily polymerize if not properly inhibited. Uncontrolled polymerization is rapid and can be very violent, generating large amounts of heat which increases the pressure. This increase in pressure causes the ejection of hot vapor and polymer which may autoignite. Explosions have been caused by uncontrolled polymerization of acrylic acid.

There have been several serious accidents over the past 25 years. In several cases, explosions due to excessive or inadvertent heating of the vessel have occurred. The overheating is often caused by improper procedures being used to thaw frozen acrylic acid. Other causes of polymerization are the removal of oxygen (oxygen is necessary to activate the storage inhibitor, MEHQ) or contamination with other chemicals.

This brochure is intended to provide essential information that should assist personnel who work with acrylic acid to avoid dangerous conditions. Prevention features should be a key part of the design and operation of acrylic acid storage facilities. The fundamental elements of a well designed storage system are: temperature control and monitoring, recirculation of the acrylic acid through a heat exchanger, use of oxygen-containing blanket gas (5 to 21 vol. %), and dedicated piping and equipment to prevent contamination. A properly designed facility must be coupled with safe operating discipline. Even a well designed system may not totally guarantee the absence of incidents. Because of factors of human error and the type of management procedures used, additional protection may be desired. Restabilization or "shortstop" systems can sometimes be used to mitigate a runaway polymerization.

Your comments and suggestions on improving this brochure are welcomed. Please contact your acrylic acid supplier to do so.

2 NAMES AND GENERAL INFORMATION

Table 2-1: Names and General Information for Acrylic Acid

Chemical Name	Acrylic Acid
Common Name	Acrylic Acid
Synonyms	Propenoic Acid Acroleic Acid Vinyl Formic Acid
CA Registry Number	79-10-7
Chemical Formula	CH_2=CHCOOH
Stoichiometric Formula	$C_3H_4O_2$
United Nations Number	UN2218

3 PROPERTIES AND CHARACTERISTICS OF ACRYLIC ACID

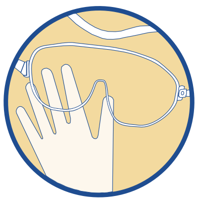
The following physical values were taken from DIPPR (Design Institute for Physical Properties) where possible. DIPPR is a subsection of AIChE and specializes in compiling physical property data banks for various chemicals.

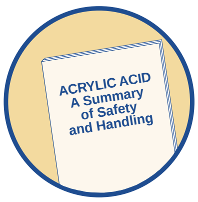
Table 3-1: Properties and Characteristics of Acrylic Acid

Properties	Values/Information	Reference/Comments
*Formula Weight	72.06	1
*Physical State	Liquid above 13°C	11, 12
Color	Clear and colorless	
Odor	Acrid	
Odor Threshold (detect)	0.092 ppm	34
*Density at 20°C 30°C	 1.05 g/mL 1.04 g/mL	2
Solubility in water in organic solvents	 Infinite Freely soluble in most solvents	
Hygroscopicity	Is hygroscopic	
*Flammable Limits (% by volume in air at 760 mm Hg)	LEL 2.4 UEL 17	10, 17, 24 10, 18, 19
Flash Point Tag Closed Cup Tag Open Cup	 50°C 54°C	
*Autoignition Temperature	412°C	10
*Boiling Point 760 mm Hg 50 mm Hg 10 mm Hg	 141°C 69°C 40°C	3, 13
Vapor Pressure 20°C	 3 mm Hg	3
*Freezing Point	13°C	11, 12
*Critical Pressure	56 atm	14
*Critical Temperature	342°C	14
Specific Gravity of Vapor (air =1)	>2.5	
*Viscosity 20°C 40°C 50°C	 1.19 cp 0.85 cp 0.73 cp	20
Heat of Combustion at 25°C	1376 kJ/g mol	16
Heat of Fusion	11.1 kJ/g mol	16
Heat of Polymerization	77.5 kJ/g mol	16
Heat of Neutralization	58.2 kJ/mol	16
Heat of Vaporization at 27°C	27.8 kJ/mol	15
Specific Heat at 25°C	2.09 kJ/kg. K	

Dissociation Constant at 25˚C	5.5 x 10^{-5}	16
Electrical conductivity	~ 1 x 10^{-3} µS/cm	23
*Thermal Conductivity 20˚C 100˚C	 0.159 W/m/K 0.136 W/m/K	21, 22
*Refractive Index at 25˚C	1.4185	2, 3
*Surface Tension at 20˚C	28.5 dynes/cm	2, 9
Dielectric Constant at 25˚C 1 kHz 100 kHz	 E = 6 E = 8	23
Electrical Group Classification (NEC)	Class I Div. II Grp. D	
Light Sensitivity	Light promotes polymerization	
Reactivity	Highly reactive both with itself and a wide variety of chemicals. Stable when properly inhibited and stored.	See Section 6
National Fire Protection Association Hazard Classification (Health, Flammability, Reactivity)	(3-2-2)	

*DIPPR values and references cited.





4 SAFETY AND HANDLING TRAINING

4.1 GENERAL CONSIDERATIONS

The safety and handling training programs established should comply with all regulations applicable to the geographic location of the facility. An example is the Occupational Safety and Health Administration's (OSHA's) Hazard Communication Standard (29 CFR 1910.1200). It is also recommended that Responsible Care® principles be considered.

All employees and contractors who handle acrylic acid should be thoroughly trained in the potential hazards, prevention techniques, emergency response plans, personal protective equipment, and environmental protection aspects which are relevant to their jobs. The use of an MSDS, the training video "Safety and Handling of Acrylic Acid," transportation pamphlets, and guidance from a supplier are suggested as training aids. Safety, health, and environmental reviews; written operating procedures; a documented training program; and written emergency response plans are all suggested.

The hazardous nature of equipment preparation and cleaning requires a qualified multifunctional team to plan each step of the job and consider all possible hazards (see Section 8). It is important that acrylic acid facilities be designed by qualified professionals who are aware of the special hazards and industry standards (see Section 7).

4.2 SAFETY, HEALTH AND ENVIRONMENTAL REVIEWS

Appropriate multifunctional teams should conduct risk assessments as part of the engineering and construction project for new or modified bulk storage and unloading facilities. It is suggested that these teams also address commissioning and start-up of the facilities. Your acrylic acid supplier can provide MSDSs, brochures, videos, and other information.

A typical review team utilizes expertise from operations, engineering, construction, technology; and safety, health, and environmental functions. The potential hazards, as well as prevention and emergency response should all be discussed by multifunctional teams and the teams should ensure appropriate documentation.

4.3 WRITTEN OPERATING PROCEDURES

Written operating procedures should give stepwise directions to employees and contractors involved in handling acrylic acid. These procedures should be written by qualified personnel and reviewed by a multifunctional team. The stepwise directions normally include concise descriptions of the hazards and environmental concerns related to each step. It is suggested that all involved personnel receive documented training on the operating procedures.

A management-of-change program should be put in place to help ensure that all changes are properly reviewed and documented before implementation.

4.4 DOCUMENTED TRAINING PROGRAM

Documented training is necessary for maintaining a good safety, health, and environmental program. An effective training program ensures that new personnel are adequately trained for their job duties and changes are communicated to those affected. Awareness of safety, health, and environmental issues should be promoted, affected personnel should have the opportunity to make suggestions, and accidents should be thoroughly reviewed.

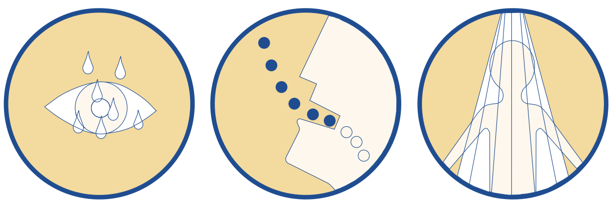
Regularly held meetings which cover safety, health, and environmental issues are an essential part of training. All related hazards, incidences, and suggestions should be periodically reviewed in these meetings and attendance should be documented.

4.5 WRITTEN EMERGENCY RESPONSE PLANS

Written emergency response plans are recommended for potential spills, fires and inadvertent polymerizations. These emergency response plans should be written by qualified personnel and reviewed by a multifunctional team. Your acrylic acid supplier may be able to provide additional information.

The written emergency response plans should be periodically reviewed and updated by a multifunctional team. These emergency response plans should be covered in safety, health, and environmental reviews and made part of the documented training program. Documented drills are suggested as part of the emergency training program. See Section 11 for information on responding to an inadvertent polymerization.

Corrective action and communication should always be addressed in the written emergency response plans. In the event of a significant incident your supplier may be able to provide advice and information. Your supplier can be reached directly or by calling CHEMTREC at 800-424-9300. CHEMTREC should always be contacted if a transport vessel is involved.



5 HEALTH AND SAFETY FACTORS

5.1 TOXICOLOGY

5.1.1 General

Acrylic acid is a liquid at room temperature and pressure. It can burn mucous membranes and possibly underlying tissues when inhaled or swallowed, even in low concentrations. Contact with the liquid can cause severe burns of the skin and/or eyes, and possibly cause permanent eye damage. The American Conference of Governmental Industrial Hygienists (ACGIH) has a threshold limit value (TLV) of 2 ppm for an eight hour time-weighted average basis with skin notation. Equilibrium concentrations of acrylic acid vapor in air at room temperature can far exceed this value.

5.1.2 Acute Exposure

Contact with acrylic acid can cause severe burns. Exposure to mists or vapor at levels above the recommended exposure limits can produce eye, nose, or lung irritation and injury. Seriousness of injury depends on the degree of exposure. The symptoms can include respiratory irritation and watering of the eyes.

Any situation in which acrylic acid contacts the eyes should be considered a medical emergency. Even dilute aqueous solutions of acrylic acid (1%) can produce serious eye injury.

5.1.3 Chronic Exposure

The main potential for human exposure to acrylic acid is by dermal contact or by inhalation. The irritating properties of the material act as a deterrent to continued exposure. Acrylic acid produces toxic effects mainly at the site of contact: nasal lesions if inhaled, skin lesions upon dermal contact, and gastrointestinal effects if acrylic acid solutions are swallowed. Overall, long-term studies and the studies for genetic and reproductive effects, indicate that acrylic acid does not pose a genotoxic or carcinogenic threat, or cause reproductive or developmental effects. The current ACGIH TLV of 2 ppm protects against potential adverse health effects.

5.2 INDUSTRIAL HYGIENE

5.2.1 General

Industrial hygiene involves the recognition, evaluation, and control of workplace health hazards. When acrylic acid is used in the workplace, it is important to evaluate the conditions of use (where, how, how often), to determine the potential for employee exposure. Since acrylic acid can be inhaled, ingested, or absorbed through the skin, each of these potential routes of exposure must be assessed and managed appropriately.

Inhalation of acrylic acid can occur when conditions cause the material to become airborne. Concentrations of acrylic acid in the air can be determined through air sampling and analysis. Air sampling results are compared to the work place exposure limit in order to determine the need for ventilation or respiratory protection. While it is recommended that acrylic acid always be used in either well ventilated areas or closed systems which can prevent occupational exposure, there may be times when this is not possible. When other control measures are not available, impractical, or fail (i.e. spill or leak), respiratory protection may be necessary to prevent exposure to airborne concentrations of acrylic acid. Respiratory protection is further addressed in Section 5.5.4.

Keeping work and break areas separate and clean should prevent accidental ingestion of acrylic acid. All food, drinks, tobacco products, and cosmetics should be kept away from chemical work areas. Once out of the area where acrylic acid is used (or stored), employees should remove all personal protective equipment, and thoroughly wash their hands and face prior to eating, drinking, smoking, or applying cosmetics.

Exposure to acrylic acid can also occur from skin contact. Skin contact can be avoided by keeping all surfaces clean and free from acrylic acid contamination, and by wearing personal protective equipment to provide a barrier between the employee and the material. Personal protective equipment includes among other items, gloves, clothing, goggles (eyes absorb most chemicals faster than other parts of the body), respirators, and footwear. The selection and use of personal protective equipment is addressed in Section 5.5 of this document.

Sound industrial hygiene practice should be built into the daily operating procedures for acrylic acid handling. It must also be applied to the non-routine events such as, spills, leaks, and other emergency situations, that can create potential for employee exposure. During non-routine events, there may not be time to initially measure acrylic acid concentrations. If acrylic acid is known to be present, but the concentration is unknown, the highest levels of personal protective equipment should be worn (self contained breathing apparatus, full body protective clothing, etc.).

The employer, acrylic acid user or handler should also establish procedures to be followed if either the ventilation equipment or personal protective equipment fails, causing the employee to come in direct contact with acrylic acid. Such procedures should include at least first aid and possibly further medical attention.

5.3 MEDICAL MANAGEMENT

Medical management should determine an employee's fitness to work with or around acrylic acid and establish procedures to be followed if an exposure incident occurs.

Two issues to be considered in the overall fitness to work with acrylic acid are vision and respiratory system capability. Employees with severely restricted, or faulty vision, should be carefully examined prior to work assignment. Contact lenses are not recommended for use in areas where there is a potential for exposure to acrylic acid. Please see Sections 5.1.2 on acute exposure and 5.5.2 on eye protection for assistance in developing policies and procedures. Since the use of respiratory protection may be required in the work area, respiratory fitness must be evaluated regularly to determine the employees' ability to wear a respirator.

5.4 FIRST AID

5.4.1 General

Every employee working in a potentially dangerous environment (with chemicals, machinery, etc.) should know a few basic first aid steps to follow in case of emergency. In the event of an emergency, it is important that the scene be surveyed to determine what occurred, and to ensure that there is no danger to self while assistance is provided. The location of all emergency eyewash stations and showers should be known. The phone number(s) to call for emergency medical services and all workplace specific emergency procedures should be readily accessible.

When providing first aid to a person who has been exposed to acrylic acid, the person should be removed from the area to prevent further exposure. The type of exposure the person has experienced should be determined – eye or skin contact, inhalation or ingestion. If possible, do not leave an injured person alone. A co-worker should be instructed to call for help while assistance is being provided to the affected individual.

In the event of an accidental exposure to acrylic acid while working alone, the worker should leave the area. After finding a co-worker and instructing him/her to call for help, the exposed worker should follow procedures to remove or dilute the contamination. Basic first aid procedures for acrylic acid exposure are given in 5.4.2 through 5.4.5.

5.4.2 Contact with Eyes

In case of eye exposure to acrylic acid at any concentration, the person should immediately go to the nearest eyewash station and flush his/her eyes with water for at least 15 minutes while holding eyelids open and away from the eyes. A physician should be contacted immediately for further medical attention. If a physician is not immediately available, the process of flushing the eyes with water should be continued for a second 15 minute period. Do not put any ointments or medications on a person's eyes unless specifically instructed by a physician.

5.4.3 Contact with Skin

If acrylic acid comes in contact with a person's skin or clothing, the individual should immediately go to the nearest safety shower and rinse off the acrylic acid. Once under the shower, all contaminated clothing and shoes should be removed. The affected area(s) of the person should be washed continuously with large quantities of water for at least 15 minutes or longer if odor persists. A physician or emergency medical services should be contacted for further assistance. No ointments or medications should be applied to the skin without specific instruction from a physician.

All contaminated clothing must be appropriately de-contaminated prior to re-use. **DO NOT TAKE CONTAMINATED ITEMS HOME FOR LAUNDERING!** If the facility is not equipped to decontaminate clothing and other items, they should be properly disposed of and replaced. **CONTAMINATED LEATHER ITEMS CANNOT BE ADEQUATELY DECONTAMINATED AND SHOULD BE DISCARDED.**

5.4.4 Inhalation

If acrylic acid vapors are inhaled, the affected person should immediately be removed from the contaminated area to a well ventilated area. Emergency assistance should be requested. Oxygen is often administered as first aid for persons who have inhaled acrylic acid. Oxygen should never be administered by untrained individuals – wait for emergency medical assistance.

5.4.4.1 Suggestions to Physicians

Oxygen has been found useful in the treatment of inhalation exposures of many chemicals, especially those capable of causing either immediate or delayed harmful effects in the lungs, such as acrylic acid. Any treatment should be carried out at the discretion of a physician.

In most exposures, administration of atmospheric oxygen at atmospheric pressure has been found to be adequate. This is best accomplished by use of a face mask with a reservoir bag of the non-rebreathing type. Inhalation of pure oxygen (100%) should not exceed one hour of continuous treatment. After each hour, therapy may be interrupted. It may be reinstituted as the clinical condition indicates.

In the event of symptoms caused from exposure to acrylic acid, or in the case of a history of severe exposure, the patient may be treated with oxygen under 0.4 kPa (4 cm [1.5 in.] of water) exhalation pressure for one-half hour periods out of every hour. Treatment may be continued in this way until symptoms subside or other clinical indications for interruption appear.

It may not be advisable to administer oxygen under positive pressure in the presence of impending or existing cardiovascular failure.

5.4.5 Ingestion

Ingestion of ***any*** quantity of acrylic acid should be treated by having the person drink large quantities of water. **DO NOT INDUCE VOMITING.** Vomiting of an acid can potentially cause burns to the esophagus and other internal organs. Immediately contact local emergency medical services or the local poison control center for assistance.

5.5 PERSONAL PROTECTIVE EQUIPMENT

5.5.1 General

Personal protective equipment (PPE) should be selected based on the potential for exposure to particular chemical(s), and the unique properties of that chemical. The Occupational Safety and Health Administration (OSHA) regulates the selection and use of PPE in 29 CFR 1910, Subpart I, Sections 1910.132-138, and Appendices A and B. In general, PPE is not an adequate substitute for appropriate workplace controls (such as ventilation), or other safe work practices. There may be situations when the only practical means of preventing employee exposure is through the effective use of PPE. When PPE is provided to employees, they must be trained in how, where, when, and why the equipment should be used. The facility must also have provisions for decontaminating and replacing such equipment as necessary.

5.5.2 Eye Protection

Eye protection in the form of chemical splash goggles should be worn to prevent acrylic acid from accidentally splashing in an employee's eye. Goggles should be non-vented, and designed specifically to protect against chemical splash. If an employee wears corrective lenses, chemical goggles should be worn over the lenses. Contact lenses are not recommended for use in areas where there is a potential for exposure to acrylic acid. Corrosive vapors can collect behind contact lenses and may cause severe damage to the eye and/or cause the contact lenses to adhere to the eyes.

5.5.3 Skin Protection

Skin protection may be found in many forms. Hand protection such as chemical resistant gloves, protective arm sleeves, aprons, full body coveralls, boots, and head coverings are among the types available. Skin protection must be made of a material impervious to acrylic acid. Butyl rubber of 0.4 to 0.6 mm thickness is a good example. Neoprene is less resistant to acrylic acid but is acceptable. Personal protective equipment should be selected on the basis of potential exposure, e.g., gloves may be required for sample collection while full body clothing including gloves, boot covers, head covering may be necessary for spill clean-up.

Skin protection for the purpose of preventing chemical exposure may be worn in conjunction with other types of PPE. For example, steel toe safety shoes may be required to prevent a person's foot from being crushed, but an additional boot cover may be required to prevent acrylic acid permeation into the safety shoe.

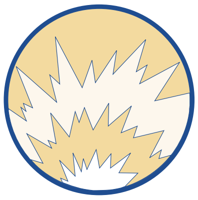
Skin protection PPE is available in a variety of sizes, and should be available in a size that fits the employee wearing it. Improperly sized PPE may compromise its effectiveness and create additional safety hazards. When skin protection PPE is used, there must be a means of cleaning or disposal/replacement of the PPE.

5.5.4 Respiratory Protection

Respiratory protection is available in two basic varieties, air purifying, and air supplied. In general, air purifying respirators provide less protection than air supplied respirators. Both types, however, have their particular advantages and limitations. The appropriate type of respirator must be selected to provide the appropriate level of protection for the anticipated degree of exposure to airborne acrylic acid (vapor or mist). Detailed guidance for the selection of respiratory protection can be found in The American National Standards Institute Document Z88.2. Respiratory protective equipment should be approved by NIOSH. It must be carefully maintained, inspected, and cleaned. All employees required to wear respiratory protection must be medically cleared to do so (this ensures their physical capability to wear a respirator) and trained to use and care for the equipment. OSHA requirements for respiratory protection can be found in 29 CFR 1910.134.

5.5.5 Head Protection

Hard hats are recommended for protection from falling objects, overhead liquid leaks, and chemical splashes.



6 INSTABILITY AND REACTIVITY HAZARDS

6.1 POLYMERIZATION

Acrylic acid is stable when stored and handled under recommended conditions. Commercially available acrylic acid is stabilized (inhibited) with hydroquinone monomethyl ether (MEHQ), which prolongs the shelf life, i.e., the time before spontaneous polymerization occurs. However, this shelf life is reduced exponentially with increasing temperature[25]. Exposure to high temperatures, therefore, must be avoided.

The polymerization of acrylic acid can be very violent, evolving considerable heat and pressure and ejecting hot vapor and polymer, which may autoignite. An explosion hazard exists due to extremely rapid pressure build up. Several case histories are known in which vessels of acrylic acid exploded due to violent ("runaway") polymerization when proper procedures were not followed.

Over the past 25 years, users of acrylic acid have collectively experienced on average one serious incident per year. In several cases, explosions due to excessive heating of the vessel have occurred. Experience has shown that overheating of acrylic acid is by far the most common cause of inadvertent polymerization. This overheating is often caused by improper procedures being used to thaw frozen acrylic acid or by heat generated by deadheaded (blocked in) pumps[26]. Other causes of polymerization are the removal of oxygen (oxygen is necessary to activate the storage inhibitor, MEHQ) or contamination with incompatible chemicals.

The presence of dissolved oxygen is necessary for MEHQ to function effectively[27-29]. Thus, acrylic acid should never be handled or stored under an oxygen-free atmosphere. A gas mixture containing 5 to 21 vol. % of oxygen at one atmosphere should always be maintained above the monomer to ensure inhibitor effectiveness. In a closed system, this atmosphere must be periodically replenished since dissolved oxygen is gradually consumed in the inhibition process, forming oligomeric peroxides. Acrylic acid being loaded into drums, rail cars, or tank trucks must have a concentration of dissolved oxygen equivalent to saturation with one atmosphere of a gas containing 5 to 21 vol. % of oxygen. Since acrylic acid is not flammable in air at ambient temperatures, air is acceptable as a blanket atmosphere. Residues in transfer lines and other stagnant areas should be blown out with a gas mixture containing 5 to 21 vol. % of oxygen. If acrylic acid is used in a facility which is not a chemical plant as defined in 29 CFR 1910.106, the use of air as a motive gas may be restricted.

If acrylic acid has been inadvertently overheated, contaminated, or over-aged, a determination of the MEHQ concentration may be desired. This analysis should be carried out by gas or high performance liquid chromatography (GC or HPLC) rather than by nitrite colorimetry (contact your supplier for method details). The nitrite colorimetric method (ASTM D-3125) erroneously identifies some MEHQ degradation products (which are not necessarily active inhibitors) as MEHQ. It must be remembered that a correct MEHQ concentration is necessary **BUT NOT SUFFICIENT** for adequate stability. Other factors influencing stability are concentration of dissolved oxygen and oligomeric peroxide content.

Good housekeeping and engineering must be exercised to strictly avoid contamination of acrylic acid. Many impurities are known that promote its polymerization, such as peroxides and peroxide-forming compounds and free-radical-generating compounds (e.g., hydroperoxides, aldehydes, ethers, azo compounds, etc.). Other classes of compounds, such as caustics, are not free radical generators, but if added to acrylic acid, can sometimes initiate thermal polymerization through their heat of neutralization. The appendix has further information on materials that are incompatible with acrylic acid.

Acrylic acid tanks should be protected from mistakenly being charged with other materials or from back flowing liquids from production vessels. This can best be achieved by using dedicated loading and unloading lines with proper identification.

A common location for inadvertent polymerization due to contamination is a "slop" container, i.e., a container for holding various waste materials to be disposed of later. Often, the chemicals added to the slop container are not monitored or controlled and the resulting mixture may contain acrylic acid and a polymerization initiator or other incompatible substance. Careful monitoring and control of materials going into the slop container will avoid this potentially dangerous condition.

In addition, care must be exercised to avoid contamination of monomer with polymerizing acrylic acid that might be present in localized or hot stagnant areas, such as deadheaded pumps, heated transfer lines, etc. Under some conditions, this material may induce the further polymerization of acrylic acid[26].

Preventing unsafe conditions through proper design and operation of acrylic acid storage facilities is the best method of avoiding an inadvertent polymerization. The fundamental elements of a well designed storage system are: temperature control, redundant temperature monitoring, recirculation of the acrylic acid through a heat exchanger, use of an oxygen-containing blanket gas, and dedicated piping and equipment. A properly designed facility coupled with a safe operating discipline will provide the user with a reliable storage system. However, even the best designed system may not totally guarantee the absence of incidents, so additional protection may be desired. Restabilization or "shortstop" systems can sometimes be used to prevent or mitigate an inadvertent polymerization[30]. See Section 11 for additional information on emergency response.

6.2 THAWING FROZEN ACRYLIC ACID

The freezing of acrylic acid should be avoided (its freezing point is 13°C [55°F]) because thawing it can be extremely hazardous. The use of insulated containers and carriers and/or tempered water tracing are recommended to prevent freezing. The temperature of the acid should be maintained at 15 to 25°C (59 to 77°F), with both high and low temperature alarms. The upper limit (of 25°C [77°F]) is to retard dimer formation, which affects the product quality but is not a safety issue (see Section 6.3).

If acrylic acid freezing occurs, the first crystals are formed along the inner wall of the container. This crystallized acrylic acid contains very little inhibitor; the inhibitor is concentrated in the remaining liquid. The temperature of the medium used to thaw acrylic acid should never be greater than 45°C (113°F).

In the event that freezing does occur, the following procedures are suggested:

- Use only tempered water, 45°C (113°F) maximum temperature, to thaw containers. **UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT OR THAW ACRYLIC ACID.** Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic acid service unless it can be ensured that the resulting maximum product temperature cannot exceed 45°C (113°F) during heating or thawing. Self-limiting or constant-wattage electrical heat tracing limited to temperatures below 65°C (149°F) and instrumented to control at ≤ 45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 45°C (113°F) may also be included as an additional safety feature to guard against failure of the tracing system. The preferred method of thawing is to recirculate the unfrozen liquid through a heat exchanger with tempered water as the heat transfer fluid. This serves to warm the mixture as well as redistribute the inhibitor and dissolved oxygen.
- The temperature of both the circulating water and the thawed portion of the monomer should be closely monitored and controlled.
- The monomer should be well mixed to redistribute the inhibitor and resupply dissolved oxygen.
- Drums of frozen acrylic acid should be thawed in a heated room at temperatures between 20 and 33°C (68 and 91°F). The drums must be agitated periodically to redistribute the inhibitor and dissolved oxygen during thawing (i.e. drum roller, tote agitator, pallet shaker). As soon as the acrylic acid is thawed, its temperature should be maintained at 15 to 25°C (59 to 77°F).
- **NEVER REMOVE LIQUID FROM A PARTIALLY-THAWED VESSEL OF ACRYLIC ACID; THE REMAINING MATERIAL COULD BE SERIOUSLY UNDER-INHIBITED.**

6.3 DIMERIZATION

Acrylic acid spontaneously dimerizes upon standing. This reaction proceeds via an ionic mechanism and no inhibitors are known to be effective for retarding or preventing it.

$$CH_2{=}CH{-}COOH \rightleftharpoons CH_2{=}CH{-}COO^- + H^+$$

Acrylic Acid Ionization

$$CH_2{=}CH{-}COO^- + CH_2{=}CH{-}COOH \longrightarrow CH_2{=}CH{-}COO{-}CH_2{-}\bar{C}H{-}COOH \xrightarrow{H^+}$$

Michael-type addition

$$CH_2{=}CH{-}COO{-}CH_2{-}CH_2{-}COOH$$

Acrylic Acid Dimer ("Diacrylic Acid")

The rate of dimer formation is temperature dependent. For example, after one month at 30°C (85°F), about 1.2% dimer is formed. At typical storage conditions, the increase in dimer concentration per hour for acrylic acid at temperature T (°K) can be estimated from the following equation[31]:

$$\text{Dimer formation rate (wt \% / hr)} = 5.055 \times 10^{12} \exp(-10808/T)$$

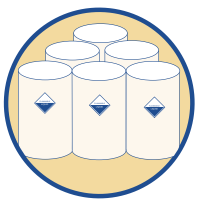
The above equation is applicable for times and temperatures leading to low dimer concentrations (e.g., less than 2%). For higher conversions of acrylic acid to dimer (longer time periods, higher temperatures), the following equation must be used[36]:

$$\text{Increase in Wt \% Dimer} = 100 - \{[0.1 + 1.401 \times 10^{11} \exp(-11027/T) \times t]^{-2}\}$$

where T is the temperature in Kelvin and t is the time in days.

The effect of water (up to 3% w/w) in acrylic acid is to accelerate the rate of dimer formation.

The formation of dimer is not hazardous but may affect the performance of the acrylic acid in some applications.



7 BULK STORAGE FACILITIES AND ACCESSORIES

7.1 GENERAL CONSIDERATIONS

The recommended bulk storage temperature range is 15 to 25°C (59 to 77°F). This temperature range avoids freezing and allows time to detect and react to a potential inadvertent polymerization. A possible product quality consideration is the rate of dimer formation, which depends on the storage temperature (see Section 6.3).

Avoid methods of heating that can generate high surface temperatures. Heat transfer fluids maintained at ≤ 45°C (113°F) can be used to heat acrylic acid containing vessels and piping systems. **UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT OR THAW ACRYLIC ACID.** Localized high temperatures can quickly initiate polymerization. Uncontrolled polymerization can be violent and may result in serious injury and/or loss of property (see Section 6.1). Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic acid service unless it can be ensured that the resulting maximum product temperature cannot exceed 45°C (113°F) during heating or thawing. Self-limiting or constant-wattage electrical heat tracing limited to temperatures below 65°C (149°F) and instrumented to control at ≤ 45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 45°C (113°F) may also be included as an additional safety feature to guard against failure of the tracing system.

Adequate inhibition is necessary to avoid polymerization in properly stored acrylic acid. The standard level of inhibitor in commercially available acrylic acid is 180-220 ppm MEHQ. In addition to the MEHQ inhibitor, the presence of dissolved oxygen in the acrylic acid liquid is essential for stabilization. Therefore, an atmosphere containing 5 to 21 vol. % of oxygen should be maintained above the acrylic acid. **NEVER USE AN INERT ATMOSPHERE.** Dissolved oxygen converts carbon centered radicals to oxygen centered radicals, which the MEHQ can trap to stabilize the acrylic acid (see Section 6.1).

Typically a 10% void volume in acrylic acid bulk storage vessels is used as a buffer against tank overflow. This also provides adequate oxygen containing gas to activate the MEHQ inhibitor.

Avoid freezing when possible. Freezing causes all impurities to concentrate in the liquid phase, potentially leaving the crystalline phase severely deficient in MEHQ inhibitor and dissolved oxygen. Section 6.2 outlines thawing procedures that should be followed in the event that freezing occurs. **NEVER REMOVE ACRYLIC ACID FROM A PARTIALLY THAWED VESSEL OR SYSTEM.** Freezing can also cause loss of circulation by plugging piping, valves and pumps which may lead to safety hazards. **NEVER TRY TO START A PUMP WHICH MIGHT CONTAIN FROZEN ACRYLIC ACID.**

Avoid condensation in vent lines and nozzles. Condensed acrylic acid can quickly polymerize due to a lack of inhibitor. Polymerization can lead to dangerous plugging of the pressure relief or vacuum relief vent system.

Take every precaution to keep acrylic acid free of contamination, for example, by using dedicated equipment and lines. Even trace contamination with an initiator can lead to a dangerous inadvertent polymerization (see Section 6.1).

Never store or handle acrylic acid in a facility without first carefully reviewing the design of all vessels and accessories for potential hazards (see Section 4.2). **NEVER STORE IN A VESSEL WHERE STEAM CAN ACCIDENTALLY HEAT THE MATERIAL DIRECTLY THROUGH A HEAT TRANSFER SURFACE OR BY DIRECT ADDITION TO THE VESSEL.** Storage in process vessels or in storage tanks designed for other chemicals can lead to unsafe conditions.

ALL ACRYLIC ACID STORAGE VESSELS (INCLUDING CHARGE OR WEIGH TANKS) SHOULD HAVE A HIGH TEMPERATURE ALARM. The purpose of this alarm is to detect an inadvertent polymerization or the introduction of excessive heat from external sources. Properly located and maintained redundant temperature probes (minimum 2) connected to a high temperature alarm can provide early warning of potentially unsafe conditions and allow for corrective action.

ALL ACRYLIC ACID PUMPS SHOULD BE PROTECTED FROM OVERHEATING. If deadheaded, many types of pumps can quickly overheat and cause a violent polymerization, which could result in serious injury and/or loss of property.

Periodically inspect vent nozzles and lines for polymer. Promptly remove any polymer found in the system. Polymer can cause plugging and may promote further polymerization under some conditions. It is good practice not to leave stagnant lines or nozzles liquid-full for over one week. Dissolved oxygen is slowly consumed and must be replenished by occasional circulation or clearing the lines with a gas containing 5 to 21 vol. % of oxygen. Depletion of oxygen can cause polymer formation and plugging.

Indoor acrylic acid storage facilities must be well ventilated to prevent local accumulation of vapors and their potential harmful effects on personnel.

7.2 DESIGN CONSIDERATIONS

Some design considerations for bulk acrylic acid storage facilities and accessories are given in Sections 7.2.1 through 7.2.12. Table 7-1 summarizes the special recommended design features covered in Sections 7.2.1 through 7.2.12. It is recommended that fail-safe positioning of automated valves and emergency backup power for critical instrumentation be included in the design. Follow all codes and regulations applicable to the geographic location of the facility. Design features of an acrylic acid storage facility are given as examples in Figures 7-1, through 7-3. Contact your acrylic acid supplier for additional guidance.

7.2.1 Temperature Control of Bulk Storage Tanks and Accessories

The installation of a reliable freeze protection system, which avoids accidental overheating of the acrylic acid, is highly recommended for all climates where freezing can occur. **THAWING FROZEN ACRYLIC ACID CAN BE EXTREMELY HAZARDOUS** (see Section 6.2).

Piping systems located outdoors (including valves, pumps and filters) should be insulated and heat-traced to avoid cold spots, which can result in plugging by frozen acrylic acid. **UNDER NO CIRCUMSTANCES SHOULD STEAM**

BE USED TO HEAT OR THAW ACRYLIC ACID. Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic acid service unless it can be ensured that the resulting maximum product temperature cannot exceed 45°C (113°F) during heating or thawing. Self-limiting or constant-wattage electrical heat tracing limited to temperatures below 65°C (149°F) and instrumented to control at ≤ 45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 45°C (113°F) may also be included as an additional safety feature to guard against failure of the tracing system. Heat transfer fluid can be used if controlled to preclude dangerous overheating as described in Section 7.1.

All storage tanks located outdoors should be insulated for freeze protection and controlled between 15 to 25°C (59 to 77°F) by a properly designed heat transfer fluid system. This temperature range prevents freezing, reduces dimer formation and provides additional time for potential emergency response. **TEMPERATURES OF 32°C (90°F) OR HIGHER CAN BE HAZARDOUS AND SHOULD BE IMMEDIATELY INVESTIGATED.** During colder months, the system can be used to avoid freezing but the heat transfer fluid must be maintained at ≤ 45°C (113°F) to avoid dangerous overheating. The heat transfer fluid can also be adjusted as needed to provide cooling during warmer weather and/or to remove heat generated by pumps. When establishing the design criteria for the heat transfer fluid system, the heat introduced during circulation by the pump should be considered as well as the potential need to control dimer formation for quality reasons (see Section 6.3). Over design of cooling can delay detection of polymerization (see Section 11).

Four commonly used temperature control systems for bulk acrylic acid tanks are given below:

1. External heat exchanger with acrylic acid tube side and heat transfer fluid on the shell side. Tank insulated and piping containing liquid acrylic acid insulated and heat-traced.
2. Heat transfer fluid circulated through a heat transfer jacket on the outside tank wall. Tank insulated and piping containing liquid acrylic acid insulated and heat-traced.
3. Heat transfer fluid circulated through a heat transfer coil inside the tank. Tank insulated and piping containing liquid acrylic acid insulated and heat-traced.
4. Tank located inside a building with a reliable heating system for freeze protection. **THE DESIGN OF INDOOR BULK STORAGE FACILITIES AND ACCESSORIES MUST ADDRESS THE SPECIAL FIRE, HEALTH AND REACTIVITY HAZARDS INHERENT TO INDOOR STORAGE FACILITIES.** All storage tanks located indoors must be vented to the outside.

7.2.2 Pumps and Protection of Pumps from Overheating

It is highly recommended that reliable engineering safeguards, such as redundant instrument interlocks, be provided to prevent accidental overheating of acrylic acid pumps. **OVERHEATING OF ACRYLIC ACID PUMPS CAN CAUSE A VIOLENT POLYMERIZATION, WHICH MAY RESULT IN SERIOUS INJURY AND/OR LOSS OF PROPERTY.** Some options to help protect pumps from overheating are given below:

- A temperature sensor placed inside the pump or close to the discharge which activates alarm and shutdown switches if a high temperature is detected. Deadheading a centrifugal pump usually causes a rapid temperature rise inside the pump (consider emergency response capabilities, see Section 11).
- A power monitor that senses a low power consumption and activates an alarm and shutdown switch. Deadheading a centrifugal pump usually results in an immediate reduction in power consumption.
- A flow detection element on the discharge line that activates an alarm and shutdown switch when a low flow is detected. A properly located low flow element connected to a shutdown switch can provide deadhead protection.
- A liquid sensor element placed in the suction line or feed vessel that activates an alarm and shutdown switch when liquid is not detected. This sensor can be used to help avoid running a pump dry but does not give deadhead protection. Many types of pumps quickly overheat if operated dry.
- Two different types of sensing elements can be installed in order to provide redundant protection from pump overheating.

Other considerations associated with pumping acrylic acid are given below:

- Double mechanical seal and magnetic drive centrifugal pumps are commonly used for acrylic acid service. These pumps require instrument interlocks to prevent dangerous overheating in case deadheading accidentally occurs.
- Seals and bearings in contact with acrylic acid should be flushed for adequate cooling and lubrication. High surface temperatures can cause polymer particles to form.
- Air driven diaphragm pumps are occasionally used for acrylic acid service. Diaphragm pumps usually stop pumping if deadheaded and may not require instrument interlocks to protect against overheating.

- Truck mounted pumps are not to be used for unloading acrylic acid unless a careful safety review has considered the potential for leaks, overheating, and contamination.
- Some guidance related to environmental protection as related to pumps is given in Section 7.2.6.

Your supplier may be contacted for additional guidance on the selection and safety of acrylic acid pumps.

7.2.3 Detecting Unsafe Conditions Inside Bulk Storage Vessels

It is highly recommended that all vessels used to store acrylic acid liquid have two independent temperature probes connected to a high temperature alarm. This includes storage tanks, check tanks, weigh vessels, and charge vessels. The two temperature probes should be located near the bottom of the vessel (preferably 90 to 180 degrees apart) and alarm in the control room in the event that either probe exceeds the high temperature set point. It is also suggested that both temperatures and rates of temperature change be monitored. These temperature probes and alarms are essential for confirming safe storage conditions and for emergency response to an inadvertent polymerization (see Section 11.1.2). Careful monitoring of temperatures and rates of temperature change is critical if unsafe conditions occur inside of a vessel. **EARLY DETECTION OF A HIGH TEMPERATURE INSIDE AN ACRYLIC ACID VESSEL CAN FACILITATE TIMELY EMERGENCY RESPONSE TO A DANGEROUS INADVERTENT POLYMERIZATION AND MAY HELP AVOID SERIOUS INJURY AND/OR LOSS OF PROPERTY.**

Frequent or continuous circulation of the vessel contents helps to prevent temperature variation within the vessel and thus gives early warning if localized heating starts. Contact your supplier for additional guidance on temperature monitoring of vessels and related emergency response.

7.2.4 Avoiding Polymer Formation in Vent Nozzles and Lines

It is recommended that precautions be taken to minimize potential condensation of acrylic acid in vent nozzles and lines. Acrylic acid condensed from vapor does not contain MEHQ stabilizer and is prone to form polymer, which can plug critical pressure and vacuum relief lines. Below are some precautions which can be taken.

1. Insulate and trace vent nozzles and lines to help keep the temperature above the dew point. For tracing, use heat transfer fluid ≤ 45°C (113°F). **UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT OR THAW ACRYLIC ACID.** Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic acid service unless it can be ensured that the resulting maximum product temperature cannot exceed 45°C (113°F) during heating or thawing. Self-limiting or constant-wattage electrical heat tracing limited to temperatures below 65°C (149°F) and instrumented to control at ≤ 45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 45°C (113°F) may also be included as an additional safety feature to guard against failure of the tracing system.
2. Nozzles which are prone to plug can be swept with a gas in order to minimize condensation. Inject some gas containing 5 to 21 vol. % of oxygen into vent nozzles. The use of dry, oil free air is suggested.
3. Slope vent lines to drain condensed liquid back to a vessel when possible and provide liquid drains where stagnant liquid pockets may develop. Polymer formation is likely in stagnant pockets of uninhibited acrylic acid.

7.2.5 Indoor Acrylic Acid Storage Facilities

All codes and regulations should be followed which are applicable to the geographic location of the facility. The special risks associated with indoor facilities should be considered during the initial project safety, health and environmental review as well as in all subsequent reviews. In particular, the consequences of spill, fire, and inadvertent polymerization should be carefully considered.

Indoor acrylic acid storage facilities must be well ventilated to prevent local accumulation of vapors, which can have potential harmful effects on personnel. It is suggested that local exhaust systems be considered to supplement the general exhaust system and that adequate air change rates are ensured. It is recommended that all laboratories be provided with a sufficient number of properly designed exhaust hoods. All indoor bulk storage tanks should vent outside of the building.

7.2.6 Engineering Features for Environmental Protection

All environmental regulations applicable to the geographic location of the facility should be met.

Spill containment helps protect public waterways and ground water. Dikes around storage tanks are used to contain spills. Properly designed dikes and flooring constructed of concrete which can hold 110% of the entire contents of the largest tank, are suggested. Spill containment for bulk unloading areas will reduce environmental risks. Concrete containment is suggested for bulk unloading areas. The use of dry disconnect fittings can reduce releases and may help avoid a spill if accidentally opened under pressure. Instrumentation to monitor the liquid level in bulk storage tanks is recommended to help prevent spills. See Section 7.2.12.

Vapor return lines are suggested for bulk unloading facilities to reduce emissions (see Section 7.2.10). If needed, scrubbers, incinerators, or thermal oxidation units can be used to control emissions. Local, state, and federal regulations may apply. Contact your supplier for additional guidance.

Magnetic drive and double mechanical seal centrifugal pumps as well as double diaphragm type pumps can reduce fugitive emissions and the risk of spills. Double mechanical seals are commercially available using a liquid (such as a glycol) or a gas (such as oil free air) as the barrier fluid. Environmental protection should be considered in the selection of pumps.

7.2.7 Engineering Considerations for Fire Control

It is highly recommended that engineering safeguards be provided for reducing the risk of an inadvertent polymerization inside of a bulk storage tank during a fire. **AN UNCONTROLLED HEAT SOURCE, SUCH AS A POOL FIRE, CAN CAUSE A VIOLENT POLYMERIZATION RESULTING IN SERIOUS INJURY AND/OR LOSS OF PROPERTY.** See Section 11 on emergency response.

Water monitors are suggested to help control acrylic acid fires and to cool acrylic acid containing equipment during a fire. Isolation with dike walls can be used to protect acrylic acid tanks from pool fires caused by other chemicals. Combustible chemicals that are not fully miscible in water can complicate fire control around an acrylic acid storage tank.

Outdoor acrylic acid bulk storage tanks should be insulated for freeze protection in most climates. This insulation should be specified as fire resistant to provide better thermal protection during a pool fire.

A foam system can be used to extinguish an acrylic acid fire (see Section 11.3).

A restabilization (shortstopping) system can be installed to allow the quick addition of phenothiazine (PTZ) in the event of a fire. Refer to Section 11.1.3 on restabilization. Acrylic acid containing PTZ is much less likely to polymerize violently during a fire.

7.2.8 Materials for Construction and Sealing in Acrylic Acid Service

Proper choice of materials of construction is important for safety, health, and protection of the environment. Some specific guidance for acrylic acid service is given below. Contact your supplier for further information.

- Material of construction is usually 304 or 316 stainless steel. Avoid contamination with alloys containing copper or silver such as brass. These metals may affect stability and may produce a color in the final product.
- Teflon® based gaskets are frequently used in a variety of applications.
- Other gasket material used in certain applications include Silicone no. 65®, EPDM, fawn Gylon®, butyl rubber, white neoprene, or Santoprene®.
- Kalrez® O-rings are used in a variety of applications.

7.2.9 Engineering Considerations for Thawing Frozen Acrylic Acid

THAWING FROZEN ACRYLIC ACID CAN BE VERY HAZARDOUS. See Section 6.2 for the hazards associated with thawing frozen acrylic acid.

Rail cars are equipped with coils that can be connected to a properly designed heat transfer fluid system. The heat transfer fluid temperature should be ≤ 45°C (113°F). See Section 9 on safe transport of acrylic acid for guidance on thawing transport vessels. Blowing residual acrylic acid into the storage tank after unloading can help minimize problems with freezing lines, valves, fittings, and hoses in cold climates. The gas used for blowing out acrylic acid systems should contain 5 to 21 vol. % of oxygen (dry oil-free air is preferred).

Some tank trucks used for transporting acrylic acid are equipped with a special in-transit heating system to prevent freezing during cold weather. Contact your supplier if a truck arrives frozen.

Bulk acrylic acid storage vessels should be equipped with external heat exchangers, internal coils or an external jacket as well as a heat transfer fluid system which maintains the heat transfer medium at ≤ 45°C (113°F). Any of the above heat transfer equipment can be used to thaw the vessel contents. Circulate the vessel contents during thawing to redistribute the inhibitor and replenish dissolved oxygen. **DO NOT REMOVE MATERIAL FROM THE SYSTEM UNTIL**

THAWING AND REDISTRIBUTION OF THE INHIBITOR AND REPLENISHMENT OF DISSOLVED OXYGEN IS COMPLETED.

Frozen piping, valves, fitting, and pumps can be safely thawed by applying tempered water which does not exceed 45°C (113°F). Thawed material should be circulated to redistribute the inhibitor and replenish dissolved oxygen. **NEVER DIRECTLY APPLY STEAM OR OTHER HIGH TEMPERATURE HEAT SOURCES TO ACRYLIC ACID CONTAINING EQUIPMENT.**

7.2.10 Venting of Bulk Storage Tanks

Follow all codes and regulations applicable to the location of the facility.

It is recommended that vacuum and pressure relief valves be installed unless the tank has an open vent to the atmosphere. A combination pressure-vacuum relief valve, sometimes referred to as a conservation vent valve, is frequently employed to help minimize the multiplicity of equipment and nozzles. Routine inspections of the conservation vent system are recommended at least once per year to remove any polymer (see Section 7.2.4) and to ensure operability. The make-up gas supplied must contain 5 to 21 vol. % of oxygen. Dry, oil-free air is preferred. The American Petroleum Institute (API) bulletin 2516 provides information related to the design and operation of conservation vents.

It is suggested that vapor return lines be installed to significantly reduce emissions during unloading or loading of transport vessels such as rail cars or tank trucks. These lines should be kept free of polymer and the vent conservation valves correctly adjusted to contain most of the vapors during unloading and loading.

IT IS ESSENTIAL THAT INCOMPATIBLE CHEMICALS NOT BE ABLE TO ENTER AN ACRYLIC ACID STORAGE TANK THROUGH THE VENT SYSTEM.

In some cases, flame arrestors are not required for acrylic acid storage tanks. Precautions should be taken to keep flame arrestors free of polymer fouling.

Storage tanks installed indoors require venting to the outside of the building.

7.2.11 Emergency Venting of Bulk Storage Tanks

All codes and regulations applicable in the geographic location in which the facility is located should be followed. Standard practice is to design storage tank emergency venting capacity for the vapor generation rate resulting from a pool fire around the tank. Guidelines can be found in OSHA standard 29 CFR1910.106 and API 2000. Relief valves, weighted pallets, quick release manway covers and rupture disks can all be used to vent the vapor directly generated by a pool fire. If used, an open vent can be sized for the pool fire case. Emergency vent devices should be inspected at least once a year to remove any polymer and to ensure operability. Storage tanks installed indoors should route the emergency vent to the outside. Contact your supplier for additional guidance.

THERE IS NO KNOWN METHOD FOR RELIABLY RELIEVING PRESSURE FROM THE MOST RAPID POLYMERIZATION OF ACRYLIC ACID IN A STORAGE TANK. See Sections 6.1 on Polymerization and 11.1.3 on Restabilization. It is suggested that weak seam roofs be used when possible in order to provide maximum venting in case of a violent polymerization.

7.2.12 Other Bulk Storage Tank Accessories

Bulk storage tanks typically have either a top entry fill pipe or a side entry nozzle for unloading and circulating the acrylic acid. Top entry fill pipes are normally tack welded to the bottom to assure static grounding and have an antisiphon hole near the top. Mixing during recirculation can be improved by locating the fill pipe across the tank from the outlet. Side entry nozzles are frequently equipped with an eductor to enhance mixing during circulation. Two eductors are sometimes installed on larger tanks. The nozzle tip should always be submerged when in use to avoid the possibility of forming a stable aerosol and ignition from static charge development. **SUBMERGED NOZZLES AND PIPES CAN PLUG IF NOT FREQUENTLY UTILIZED.**

Level monitoring instrumentation is recommended to avoid spills when filling a storage tank. A 10% minimum void volume of oxygen containing blanket gas should be maintained above the liquid. Ensure that the inlet nozzle or eductor is submerged in liquid. It is recommended that this level monitoring instrumentation include device(s) which alarm if the tank is filled above or emptied below a safe level. Many tanks are also equipped with a high-high level switches, which shuts off the unloading pump before a potential spill. A differential pressure level indicator (bubble type) is frequently used in acrylic acid service. A gas containing 5 to 21 vol. % of oxygen must be used for bubble type level indicators. Dry, oil-free air is preferred for this service.

Safety showers and eye bath stations are recommended in the unloading and storage tank areas. Take precautions to prevent freezing in these stations as dictated by the local climate.

7.2.13 Summary of Special Recommended Design Features for Bulk Acrylic Acid Storage Facilities and Accessories

Table 7-1 summarizes the special recommended design features for bulk acrylic acid storage facilities and accessories. The table also includes references to the related information given in Sections 7.2.1 through 7.2.12.

Table 7-1: Summary of Special Recommended Design Features for Bulk Acrylic Acid Storage Facilities and Accessories

FEATURE	SECTION REFERENCE
Install a reliable freeze protection system which avoids accidental overheating of the acrylic acid (applies to both outdoor and indoor facilities).	7.1, 7.2.1, 7.2.9
Insulate and trace outdoor piping systems unless located in a climate which precludes freezing of acrylic acid.	7.1, 7.2.1, 7.2.9
Never provide high temperature heat sources such as steam or uncontrolled electric elements for direct heating of acrylic acid.	7.1, 7.2.1, 7.2.4, 7.2.9
Install two independent temperature probes on all bulk acrylic acid storage vessels for monitoring the temperature, rate of temperature change and for activating an alarm in the event of a high temperature excursion.	7.1, 7.2.3
Provide reliable engineering safeguards such as redundant instrumentation interlocks to prevent accidentally overheating of acrylic acid by pumps.	7.1, 7.2.2
Take precautions to limit the temperatures of pump seals and bearings in contact with acrylic acid.	7.2.2
Provide the capability of circulation in bulk acrylic acid storage tanks.	7.1, 7.2.1, 7.2.3, 7.2.9
Provide gas containing 5 to 21vol. % of oxygen (dry, oil-free air is preferred) for blanketing acrylic acid storage vessels and for blowing out acrylic acid lines.	7.1, 7.2.4, 7.2.9, 7.2.10, 7.2.12
Take precautions to minimize potential condensation of acrylic acid in vent lines. This can cause polymer formation resulting in plugged pressure and/or vacuum relief lines.	7.1, 7.2.4, 7.2.10, 7.11
Provide engineering safeguards to reduce the risk of a violent inadvertent polymerization inside an acrylic acid bulk storage tank during a fire.	7.1, 7.2.5, 7.2.7
Design bulk acrylic acid storage facilities and accessories to minimize the risk of an accidental contamination.	7.1, 7.2.10
Design the piping systems to minimize stagnant pockets of acrylic acid which may result in polymerization.	7.1, 7.2.4, 7.2.9
When applicable, address the special reactivity, fire and health hazards inherent to indoor facilities.	7.1, 7.2.1, 7.2.5, 7.2.10, 7.2.11

Table 7-2: Key to Symbols in Figures 7-1, 7-2, 7-3, 11-1 and 11-2

Symbol	Definition
DTAH	Temperature change alarm - high
FAL	Flow alarm - low
FE	Flow element
FI	Flow indicator
FIC	Flow indicator/controller
FY	DCS calculation block circuitry
FQ	Flow totalizer
HE	Heat exchanger
I	Interlock
JAL	Power alarm - low
JR	Power recorder
JSL	Power switch - low
JT	Power transmitter
LAH	Level alarm - high
LAL	Level alarm - low
LALL	Level alarm - low low
LG	Level gauge
LI	Level indicator
LSHH	Level switch - high high (shuts down unloading pump)
PI	Pressure indicator
PIC	Pressure indicator and control
PVRV	Pressure and vacuum relief valve
TAH	Temperature alarm - high
TAHH	Temperature alarm - high high
TAL	Temperature alarm - low
TC	Temperature control
TE	Temperature element
TI	Temperature indicator
TR	Temperature recorder
TSH	Temperature switch - high (shuts down pump)
V	Vessel

Figure 7-1: Example of an Acrylic Acid Storage Facility

The example illustrates some of the safety features discussed in the booklet. Not all equipment or instrumentation required for operability is shown. See Table 7-2 for key to symbols.

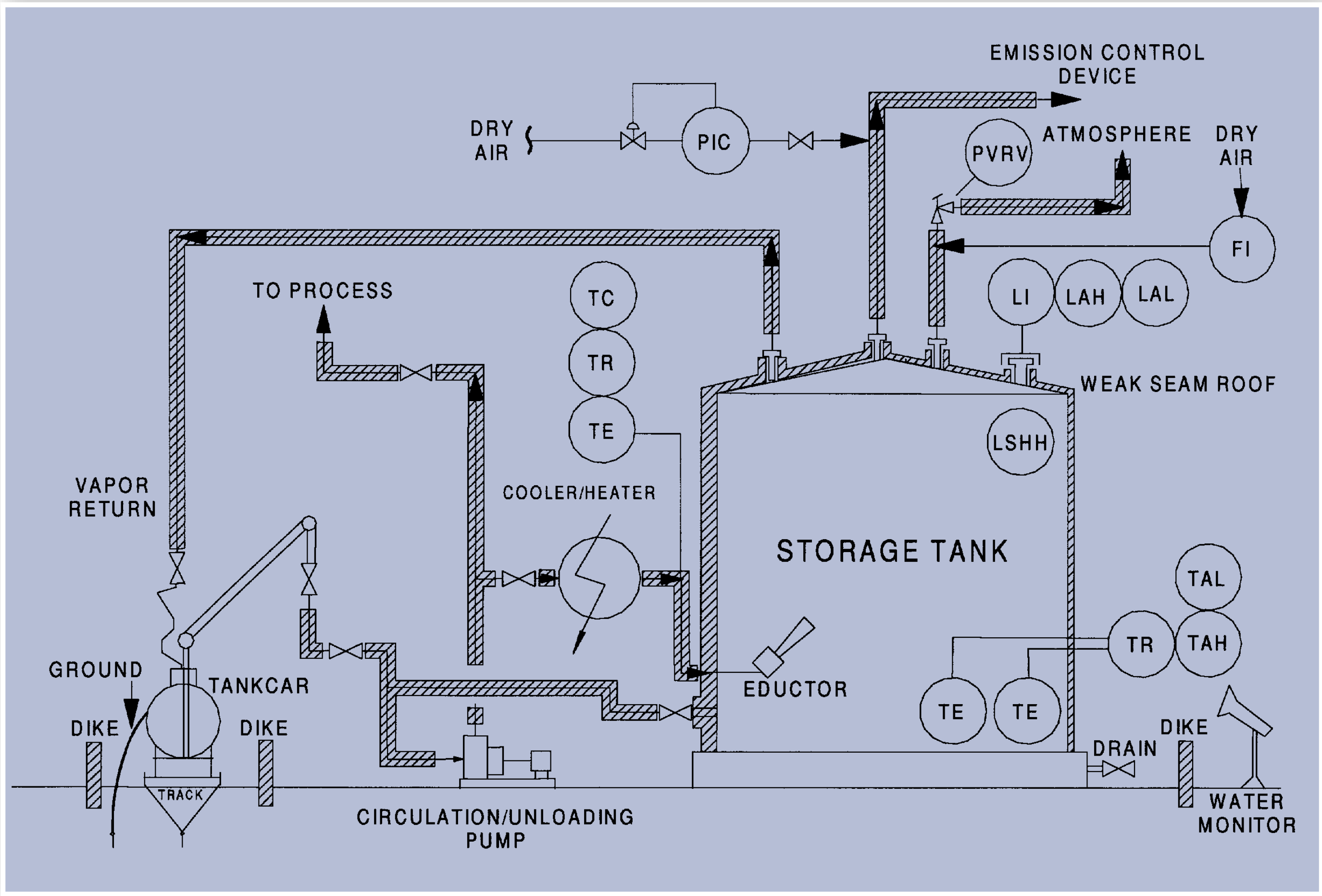


Figure 7-2: Example of an Acrylic Acid Storage Tank Temperature Control System

This example illustrates some of the safety features discussed in this booklet. Not all equipment or instrumentation required for operability is shown. See Table 7-2 for key to symbols.

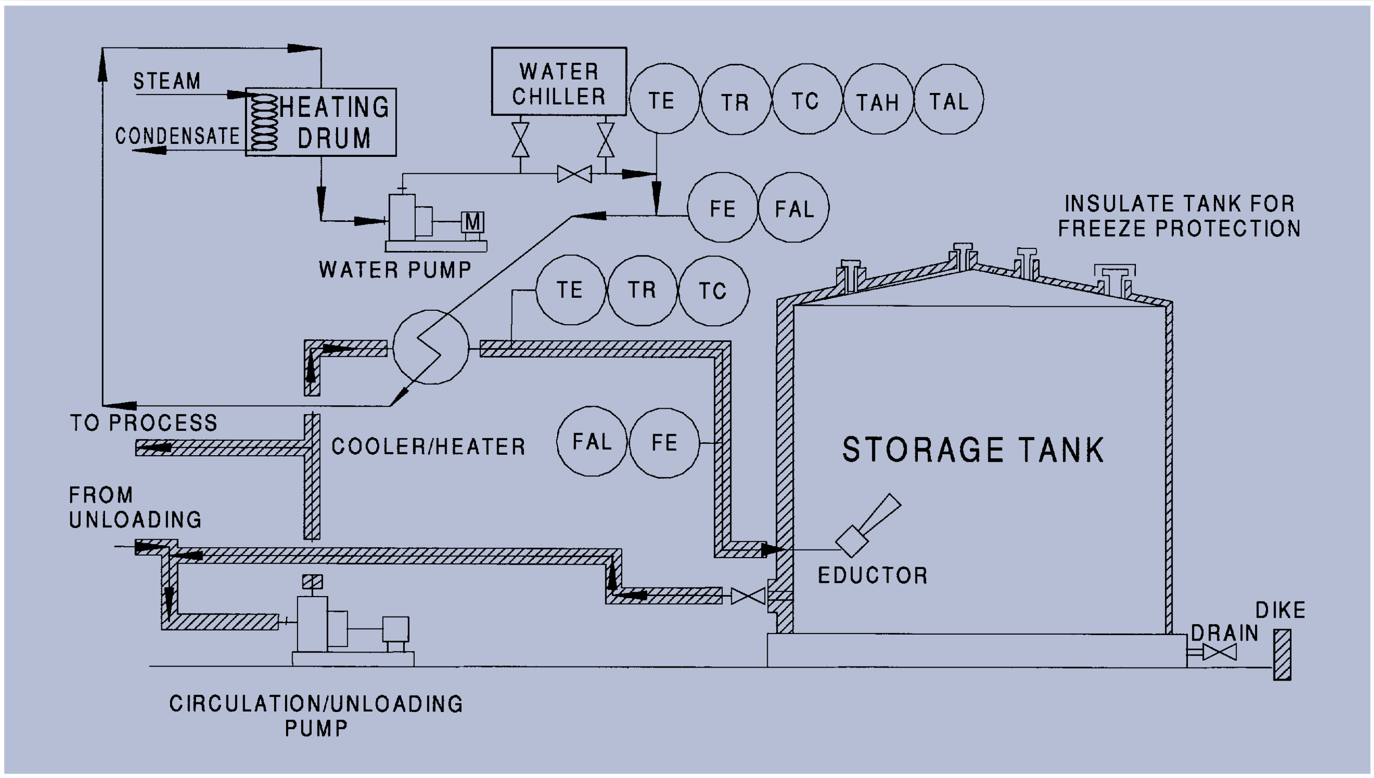
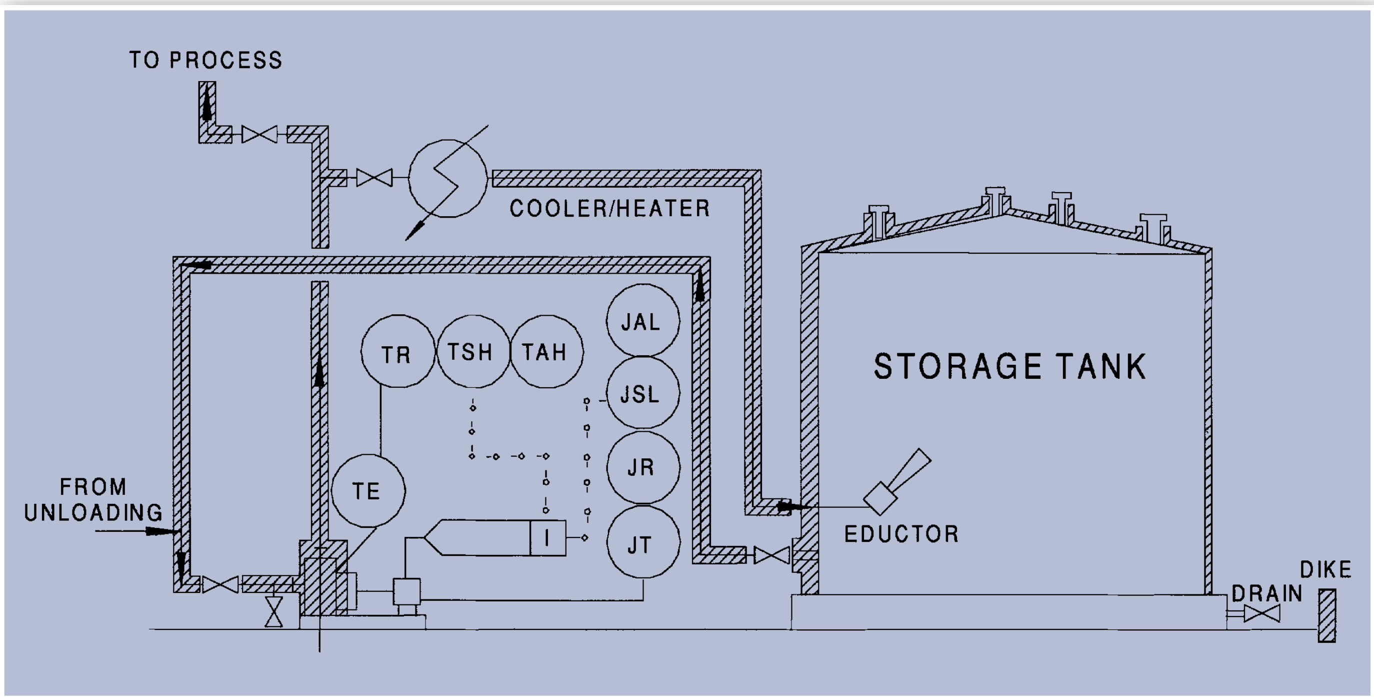
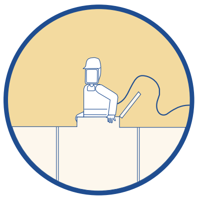


Figure 7-3: Example of an Acrylic Acid Pump Loop

This example illustrates some of the safety features discussed in this booklet. Not all equipment or instrumentation required for operability is shown. See Table 7-2 for key to symbols.





8 EQUIPMENT PREPARATION AND CLEANING

8.1 GENERAL CONSIDERATIONS

The hazardous nature of equipment preparation and cleaning require that a qualified multifunctional team plan each step of the job in detail and consider all possible hazards. This team should ensure that stepwise safe work procedures are written which clarify hazards, preventive measures and personal protective equipment to be worn at each step.

Equipment preparation and cleaning should be done under the direction of trained personnel who are familiar with the written stepwise safe work procedures. All involved personnel should understand the potential hazards pertaining to the job before work is initiated.

8.2 COMMISSIONING ACRYLIC ACID BULK STORAGE FACILITIES

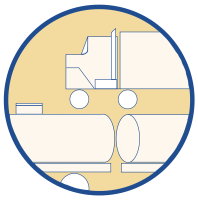
The following are the typical steps included in standard operating procedures for commissioning acrylic acid bulk storage facilities:

- Break all flanges at equipment. Do not flush through instruments, pump and exchangers.
- Water flush all lines then re-assemble equipment.
- Fill tank with high-purity water checking all possible instrumentation interlocks.
- Perform water run. Run as much of the system as possible to identify problems and tune control loops.
- Drain water from tank and blow/drain all lines.
- When dry, the system is ready to receive product.
- The blanket gas must contain 5 to 21 vol. % of oxygen.
- Do not use incompatible substances, such as nitric acid, for preparing acrylic acid systems. See Section 6.1 on Polymerization and the appendix on Incompatible Materials (Section 13.1). Contact your acrylic acid supplier if additional guidance is needed.

8.3 CLEANING ACRYLIC ACID BULK STORAGE FACILITIES FOR DE-COMMISSIONING

The following are the typical steps included in standard operating procedures for cleaning acrylic acid bulk storage facilities for de-commissioning:

- Blow all product from lines and accessories into tank using a gas with 5 to 21 vol. % of oxygen. Air is preferred. Take precautions not to damage any sensitive equipment.
- Remove product from the tank.
- Flush all lines and accessories with water.
- Steam all lines and accessories until clean. Take precautions not to damage any sensitive equipment or seals.
- Open tank and steam if odor is found. Take precautions not to damage any sensitive equipment or seals.
- Caustic wash with 5 to 8% caustic if soft polymer is found. Remove caustic solution and rinse thoroughly with water.
- Blast with high pressure water or grit if hard polymer is found. Consider testing integrity of the tank after blasting.
- The tank must be free of odor and tested for flammable vapors, oxygen content and residual caustic (if used) before entering. Follow all applicable regulations concerning vessel entry.
- Dispose of any residual product, polymer, cleaning solutions and rinse solutions at approved facilities.



9 SAFE TRANSPORT OF ACRYLIC ACID

9.1 PERSONAL PROTECTIVE EQUIPMENT FOR LOADING AND HANDLING

Full protective clothing should be considered as follows: a chemical resistant splash suit, gloves, boots, eye protection, and respiratory protection. Clothing made of supported neoprene, neoprene, or other suitable material should be worn to protect the body against accidental acrylic acid splashes. Contact lenses substantially increase the risk of damage to eyes and, if your policies permit, should only be worn with special precautions. Full eye protection should include plastic shields with forehead protection in addition to chemical splash goggles. Respiratory protective equipment should be a type approved by NIOSH.

9.2 GENERAL CONSIDERATIONS

The following are general considerations that apply to all modes of transportation for acrylic acid. Also see Section 6 for Instability and Reactivity Hazards

- Acrylic acid must be stored in an oxygen-containing atmosphere. The MEHQ inhibitor is not effective in the absence of oxygen.
- Do not use pure oxygen for sparging, blowing lines, or blanketing. Pure oxygen could create a fire hazard.
- Do not use pure nitrogen or any other inert gas for sparging, blowing lines, or blanketing. Pure nitrogen or other oxygen-free gas could reduce the dissolved oxygen to a dangerously low level where the effectiveness of the inhibitor could be greatly reduced.
- Air or a gas mixture with 5 to 21 vol. % of oxygen is preferred for use in handling acrylic acid.
- Cleanliness is essential. All containers should be free of contamination.
- Avoid overheating of acrylic acid. **UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT OR THAW ACRYLIC ACID.** A proper fail-safe tempered water system or a warm room [45°C (113°F) maximum] should be used for these purposes. Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic acid service unless it can be ensured that the resulting maximum product temperature cannot exceed 45°C (113°F) during heating or thawing. Self-limiting or constant-wattage electrical heat tracing limited to temperatures below 65°C (149°F) and instrumented to control at ≤ 45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 45°C (113°F) may also be included as an additional safety feature to guard against failure of the tracing system.
- Acrylic acid is classified as "Corrosive, Flammable Liquid" as defined in DOT regulations Section 172.101. As such, it must be packed in DOT specification containers when shipped. The IMDG classification is "Corrosive, Flammable." International shipping requirements should be reviewed to determine compatibility with United States and IMDG requirements.
- ICSHAM suppliers adhere to all regulations concerning free air space (outage) in filled containers. DOT requires that drums must be filled so that they will not be liquid full at 54°C (130°F). This corresponds to about 3% void space (outage) at 25°C (77°F). DOT requires that bulk containers must be loaded so that they have at least 1% void volume at 46°C (115°F) for uninsulated tanks and at 41°C (105°F) for insulated tanks. Samples should adhere to the minimum void space requirements for drums. Please keep in mind that temperatures above 25°C (77°F) are not recommended for long-term storage. **PRODUCT TEMPERATURES OF 32°C (90°F) OR HIGHER CAN BE HAZARDOUS AND SHOULD BE IMMEDIATELY INVESTIGATED.**
- Retained samples should be stored for no more than a year in a cool dark place. Plastic-Coated amber glass bottles are available and are recommended for handling and storing small amounts of acrylic acid.
- Non-Bulk Performance Oriented Packaging Standards in DOT 49 CFR 178.500 require testing of non-bulk acrylic acid shipping containers for Hazard Class 8, Packing Group II. Your sample container supplier can perform testing and guarantee conformance to DOT requirements.

Containers that may test acceptably to DOT requirements for land transportation include the following:

- 1 - Gallon or less
  - Amber glass or polyethylene jug or bottle with screw cap and polyethylene insert with DOT approved outer packaging (reference 49 CFR 173.202).
- 5 - Gallon
  - UN 1H1, high density polyethylene drum.

9.3 TRANSPORTATION INCIDENTS - IMMEDIATE ACTIONS

IN THE EVENT OF A SPILL, FIRE OR SUSPECTED POLYMERIZATION, IMMEDIATELY CALL CHEMTREC AT 1-800-424-9300. CHEMTREC will contact the supplier.

In the event a shipping container (rail car, tank truck, drum, intermediate bulk container [IBC/tote]) or its contents becomes damaged so that delivery to destination cannot proceed safely, every effort should be made to park the vehicle where it will not endanger traffic or property, if possible in a vacant lot away from populated areas. The police and fire departments should be notified and the public should be restricted from the area. Immediately contact CHEMTREC at 800-424-9300. CHEMTREC will contact the supplier. Follow precautions stipulated in the supplier's MSDS for acrylic acid. See Section 11 on Emergency Response for additional information.

9.4 TRUCKS

The use of tank trucks for bulk transport of acrylic acid is authorized by DOT. Authorized bulk containers are described in DOT regulations 49CFR 173.243. Refer to this section for complete bulk packaging information, including special requirements.

DOT approved containers include the following:

- Tank Truck
  - Stainless steel or aluminum, coiled and insulated with DOT specification MC-304, MC-307, MC-310, MC-311, MC-312, MC-330, MC-331, DOT-407 or DOT-412.

Apply the DOT "Corrosive", UN2218, Hazard Class 8 placards to Tank Trucks.

DOT Hazardous Materials Regulations are contained in 49 CFR 100-180. Please consult these and/or local regulations for complete, up to date, tank truck specification packaging and placarding requirements.

9.4.1 Carrier information

The shipper is responsible for providing trucks that meet all guidelines for safe transport of acrylic acid, inhibition of the product and proper temperature for shipping. The empty trailer should be < 38°C (<100°F) before loading with acrylic acid. Tank trucks used for transporting acrylic acid are equipped with a special in transit heating system to prevent the product from freezing during cold weather. Acrylic acid freezes at 13°C (55°F). The temperature of the acrylic acid should be controlled between 15°C and 25°C (59°F and 77°F) by use of a captive tempered glycol-water system. The upper temperature limit (of 25°C [77°F]) is necessary to retard dimer formation. **TEMPERATURES OF 32°C (90°F) OR HIGHER CAN BE HAZARDOUS AND SHOULD BE IMMEDIATELY INVESTIGATED.** The captive glycol-water system is heated by the tractor's radiator water by means of a separate trailer mounted exchanger. The temperature of the captive glycol-water mixture should not exceed 45°C (113°F). **DIRECT HEATING OF THE ACRYLIC ACID WITH TRACTOR RADIATOR WATER IS NOT ACCEPTABLE DUE TO ITS HIGH TEMPERATURE.**

Drivers should be thoroughly trained in the operation of the heating system, and should be able to recognize when the system is not working properly. To ensure reliable operation, the temperatures of both the product and the glycol-water should be monitored. In transit, the truck driver should log the temperature of the acrylic acid once every 4 hours until the delivery is made. The customers will be shown this log at the time of delivery. Product should not be offered for delivery if the temperature is less than 15°C (59°F) without approval of the shipper. **IF AT ANY TIME THE TEMPERATURE OF THE ACRYLIC ACID REACHES 32°C (90°F) OR ABOVE, OR HAS A TEMPERATURE RISE OF 2°C (4°F) PER HOUR, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300.** CHEMTREC will contact the supplier. High temperatures can be a warning sign or indicator of a possible inadvertent polymerization. High temperatures can cause an inadvertent polymerization and must be taken seriously. The truck should be isolated as dictated by the circumstances and conditions at the time. Also see Section 6 on instability and reactivity hazards and Section 11 on emergency response for more details.

9.4.2 Thawing

Thawing of frozen acrylic acid can be extremely hazardous if proper procedures are not followed. Acrylic acid can be safely thawed by circulation of tempered water through heating coils. The temperature of the water should not exceed 45˚C (113˚F). **UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT OR THAW ACRYLIC ACID.** Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic acid service unless it can be ensured that the resulting maximum product temperature cannot exceed 45˚C (113˚F) during heating or thawing. Self-limiting or constant-wattage electrical heat tracing limited to temperatures below 65˚C (149˚F) and instrumented to control at ≤ 45˚C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at (45˚C (113˚F) may also be included as an additional safety feature to guard against failure of the tracing system.

NO MATERIAL SHOULD BE REMOVED FROM A PARTIALLY FROZEN OR THAWED TANK TRUCK. Such material may be uninhibited or contain most of the inhibitor required for the entire contents of the tank truck. The acrylic acid should be mixed thoroughly during and after thawing to assure uniform mixing of the inhibitor and dissolved oxygen before any liquid is withdrawn. During thawing, proper venting (such as open manway hatch with a vapor recovery bonnet) should be provided. As soon as the material is thawed, the temperature should be maintained between 15˚C and 25˚C (59˚F and 77˚F). The upper temperature limit (of 25˚C [77˚F]) is necessary to retard dimer formation.

9.4.3 Unloading

The following procedures are suggested to reduce the risks during the unloading of acrylic acid. The contents of the truck must be ***positively identified*** before they are transferred. If sampling is required, refer to site specific procedures. Continuous monitoring of the unloading process is appropriate. Acrylic acid is a corrosive liquid and should be handled accordingly.

An emergency shower and eye wash station should be directly accessible from and within 8 meters (25 ft) of the unloading spot and other sources of water should be available for wash downs. The emergency shower and eye wash station should be tested periodically to ensure that they function properly. Personal protective equipment should be worn while sampling or making any connections.

Proper equipment should be used to protect against spills. The piping for unloading should be on continuous circulation or arranged so the acrylic acid will drain toward the storage tank when transfer is stopped. Where necessary, a check valve should be provided on the unloading hose to ensure that total tank contents will not spill in the event of a hose break. The pump glands, flanged fittings and valve stems should be provided with splash collars in cases where personnel could be exposed to major acrylic acid leaks or sprays.

9.4.3.1 Pumping Trucks with Closed Loop System

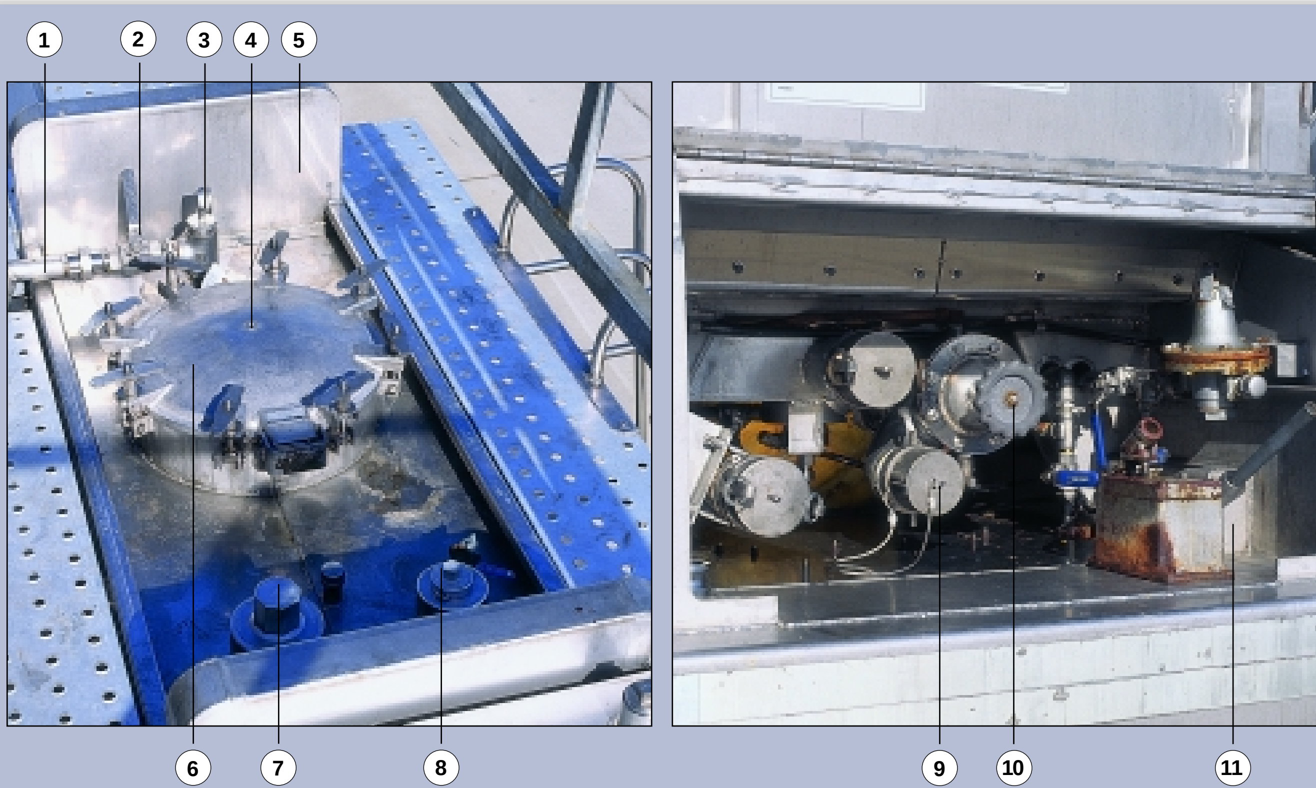
The suggested method for unloading a tank truck is by pumping with a closed loop (vapor balance) system in which the vapors are returned to the tank truck, or sending the vapors to a scrubber or incinerator. The numbers in parenthesis below correspond to hoses, valves, lines, etc., associated with the unloading procedure and are pointed out in Figure 9-1.

1. Spot the trailer and set wheel chocks. The engine should be stopped and the emergency breaks applied during unloading.
2. Connect tank truck grounding.
3. Check that the temperature of the truck is less than 32˚C (90˚F) before unloading. Verify that the receiving vessel will hold the entire contents of the tank truck. The acrylic acid receiving vessel needs to be less than 25˚C.
4. Open top vapor (vent) valve (8).
5. Connect vapor hose and open valve (7) to equalize pressure and confirm all vapor valves and lines are clear.
6. Connect liquid line (9) and open external (secondary) valve (10).
7. Open internal valve by using hydraulic pump and handle (11).
8. Start pump. Once flow has started, continue to monitor tank truck vapor return line and gauge to confirm flow and to avoid pulling a vacuum that may implode truck.
9. To avoid freezing of acrylic acid in discharge hose, flow should not be interrupted.
10. When the trailer is empty, shut off pump and close all valves (10 & 11).
11. Depressure line, drain and disconnect hose (9), and replace cap.
12. Block in vapor system valves at (8) on tank truck and at ground level if equipped, remove hose, and replace caps.
13. Close and secure housings. Leave placards in place. Follow DOT guidelines for securing truck before shipment.

14. Disconnect ground and remove wheel chocks.
15. Verify that truck is empty. If truck cannot be emptied, notify shipper before returning the truck.

For additional information see the ICSHAM pamphlet, "Transportation of Acrylic Acid by Tank Truck."

Figure 9-1: Acrylic Acid Tank Trucks



1. Ground level/vapor pressure supply valve and fitting 1 1/2" Camlock with 3/4" Chicago (Crowsfoot) adapter
2. 1/4 turn top vapor (vent) valve
3. Xmas tree with valve and gauge
4. Clean out cap
5. Rollover protection and protective housing for vapor/pressure supply valve at the top of the tank
6. Manway
7. Vacuum relief valve
8. Pressure relief valve
9. Rear discharge with quick disconnect fittings and dust cap installed
10. External (secondary) discharge valve
11. Hydraulic pump and handle to operate internal valve

9.4.3.2 Unloading Trucks With Pressure

An alternate method for unloading is to pressure the acrylic acid by using a gas containing 5 to 21 vol. % of oxygen. The inhibitor, MEHQ, requires oxygen to prevent polymerization. The pressure of the unloading gas should be regulated below 80% of the safety valve setting. The numbers in parenthesis below correspond to hoses, valves, lines, etc., associated with the unloading procedure and are pointed out in Figure 9-1.

1. Spot trailer and set wheel chocks. The engine should be stopped and the emergency breaks applied during unloading.
2. Connect tank truck grounding.
3. Verify that the receiving vessel will hold the entire contents of the tank truck. Check that the temperature of the truck is less than 32˚C (90˚F) before unloading.
4. Open top vent valve (8).

5. Connect pressure supply hose and open vapor valve (7).
6. Open pressure supply hose valve enough to keep a positive pressure on the tank truck and confirm all vent valves and lines are clear.
   Regulate the unloading gas pressure so that it does not exceed 80% of the safety valve set pressure of the tank truck.
7. Connect liquid line (9) and open external (secondary) valve (10).
8. Open internal valve by using hydraulic pump and handle (11).
9. To avoid freezing of acrylic acid in discharge hose, flow should not be interrupted.
10. When the trailer is empty, block in all valves.
11. Depressure line, drain and disconnect hose (9), and replace cap.
12. Block in pressure supply system valve at ground level if equipped and/or on top (8), remove hose, and replace caps.
13. The receiving site may require that the truck be depressured. Vent the truck down to minimal pressure before returning it to the shipper. If the truck cannot be depressurized, add a tag stating "Truck under pressure."
14. Close and secure housings. Leave placards in place. Follow DOT guidelines for securing truck before shipment.
15. Disconnect ground and remove wheel chocks.
16. Verify that truck is empty. If truck cannot be emptied, notify shipper before returning the truck.

This procedure will work to pressure directly to storage tank as well as to pressure to a pump. For additional information see the ICSHAM pamphlet, "Transportation of Acrylic Acid by Tank Truck."

9.5 RAIL CARS

The use of rail cars for bulk transport of acrylic acid is authorized by DOT. Authorized bulk containers are described in DOT regulations 49CFR 173.243. Refer to this section for complete bulk packaging information, including special requirements.

DOT approved containers include the following:

- Rail Car
  - DOT Class 103, 104, 105, 106, 109, 110, 111, 112, 114, 115 or 120
    - Stainless steel with stainless steel interior, unlined.
    - Aluminum, non-flammable with aluminum interior, unlined.
    - Aluminum, flammable with aluminum interior, unlined.

The car must have a stainless steel eductor pipe, gauging device, thermometer well, and insulation. It is also recommended that the car be equipped with coils which could be used for tempered water for thawing or cooling if necessary.

DOT Hazardous Materials Regulations are contained in 49 CFR 100-180. Please consult these and/or local regulations for complete up to date rail car specification, packaging, and placarding requirements. The DOT "Corrosive," UN2218, Hazard Class 8 placards should be applied to rail cars.

9.5.1 Carrier Information

The shipper is responsible for providing rail cars that meet all guidelines for transport of acrylic acid, inhibition of the product, and proper temperature for shipping. Temperature measurement of the product in transit via rail is not mandated and rarely is done. However, **SHOULD AN INCIDENT OCCUR, SUCH AS AN ACCIDENT INVOLVING THE CAR, AN ELEVATION IN TEMPERATURE OF THE RAIL CAR CONTENTS, A STRONG ODOR IS NOTED, OR PERSONNEL NEAR THE CAR SUSPECT THE ACRYLIC ACID IN THE CAR IS POLYMERIZING, IMMEDIATELY CONTACT CHEMTREC AT 1-800-424-9300.** CHEMTREC will contact the supplier. High temperatures and venting can be a warning sign or indicator of a possible inadvertent polymerization. High temperatures can cause an inadvertent polymerization and must be taken seriously. The car should be isolated as dictated by the circumstances and conditions at the time. Also see Section 6 on instability and reactivity hazards and Section 11 on emergency response for more details.

9.5.2 Thawing

Thawing of frozen acrylic acid can be extremely hazardous if proper procedures are not followed. Frozen acrylic acid in a rail car can be safely thawed by circulation of tempered water through the heating coils. The temperature of the water should not exceed 45°C (113°F). **UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT OR**

THAW ACRYLIC ACID. Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic acid service unless it can be ensured that the resulting maximum product temperature cannot exceed 45°C (113°F) during heating or thawing. Self-limiting or constant-wattage electrical heat tracing limited to temperatures below 65°C (149°F) and instrumented to control at ≤ 45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 45°C (113°F) may also be included as an additional safety feature to guard against failure of the tracing system.

NO MATERIAL SHOULD BE REMOVED FROM A PARTIALLY FROZEN OR THAWED RAIL CAR. Such material may be uninhibited or contain most of the inhibitor required for the entire contents of the tank car. It should be mixed thoroughly during and after thawing to assure uniform mixing of the inhibitor before any liquid is withdrawn. During thawing, proper venting (such as open manway hatch with a vapor recovery bonnet) should be provided. As soon as the material is thawed, the temperature should be maintained between 15°C and 25°C (59°F and 77°F). The upper temperature limit (of 25°C [77°F]) is necessary to retard dimer formation.

9.5.3 Unloading

The following procedures are suggested to reduce the risks during the unloading of acrylic acid. The contents of the tank car should be ***positively identified*** before they are transferred. If sampling is required, refer to site specific procedures. Continuous monitoring during unloading is appropriate. Acrylic acid is a corrosive liquid and should be handled accordingly.

An emergency shower and eye wash station should be directly accessible and within 8 meters (25 ft) of the unloading spot, and other sources of water should be available for wash downs. The emergency shower and eye wash should be tested periodically to ensure that they function properly. Personal protective equipment should be worn while sampling or making any connections.

Proper equipment should be used to ensure against spills. The piping for unloading should be on continuous circulation or arranged so the acrylic acid will drain toward the storage tank when transfer is stopped. Where necessary, a check valve should be provided on the unloading hose to ensure that total tank contents will not spill in the event of a hose break. The pump glands, flanged fittings and valve stems should be provided with splash collars in cases where personnel could be exposed to major acrylic acid leaks or sprays.

9.5.3.1 Pumping Rail Cars with Closed Loop System

The suggested method for unloading a tank car is by pumping with a closed loop (vapor balance) system in which the vapors are returned to the tank car, or by sending the vapors to a scrubber, or vapor incinerator. If the tank car is used to collect the vapors, the shipper must be notified that the tank car contains product vapors under pressure. Please refer to the ICSHAM pamphlet "Transportation of Acrylic Acid by Rail Car" for additional information.

1. Ensure that the hand brake is set, the wheels are chocked, and "tank car connected" sign is in place on the track. Derailers should be in place or switches locked out.
2. Connect the ground cable to the tank car.
3. Verify that the receiving vessel will hold the entire contents of the rail car.
4. On the top of the tank car, remove the seal pin on the eduction equipment cover and open cover. If temperature indication is available, check that the temperature of the car is less than 32°C (90°F) before unloading.
5. Examine all valves to be certain that they are closed before removing caps, plugs, or flanges.
6. Connect vapor hose to vent valve on tank car and open valves to equalize pressure and confirm all vapor valves and lines are clear.
7. Connect unloading line to the eduction valve, or if unloading from the bottom, the bottom outlet valve.
8. Close all bleeds on the unloading line and open the eduction valve, or if bottom unloading, open the bottom outlet secondary valve, then open the bottom outlet valve.
9. Start pump. Once flow has started, continue to monitor tank car vapor return line and gauge to confirm flow to avoid imploding the tank car.
10. To avoid freezing of acrylic acid in discharge hose, flow should not be interrupted.
11. When the tank car is empty, shut off pump and close all valves.
12. Depressure unloading line, drain and disconnect the hose and fittings.

13. Block in vapor system valve and vent valve on the tank car. Depressure and disconnect hose.
14. Re-install all flanges and plugs removed. Close and secure all housings. Follow DOT guidelines for securing rail car before shipment.
15. Per DOT regulations at the time of this publication, placards are **NOT** to be reversed.
16. Disconnect electrical ground and remove wheel chocks. Remove "tank car connected" sign, remove derailers, and unlock switches.
17. Verify that tank car is empty. If tank car cannot be emptied, notify shipper before returning the tank car.

9.5.3.2 Unloading Rail Cars with Pressure

An alternate method for unloading is to pressure the acrylic acid by using a gas containing 5 to 21 vol. % of oxygen. The inhibitor, MEHQ, requires oxygen to prevent polymerization. The pressure of the unloading gas should be regulated below 80% of the safety valve setting. This procedure will work to pressure directly to a storage tank as well as to pressure to a pump. If the tank car is used to collect the vapors, the shipper must be notified that the tank car contains product vapors under pressure. Please refer to the ICSHAM pamphlet "Transportation of Acrylic Acid by Rail Car" for additional information.

1. Ensure that the hand brake is set, the wheels are chocked, and "tank car connected" sign is in place on the track. Derailers should be in place or switches locked out.
2. Connect the ground cable to the tank car.
3. Verify that the receiving vessel will hold the entire contents of the rail car.
4. On the top of the tank car, remove the seal pin on the eduction equipment cover and open cover. If temperature indication is available, check that the temperature of the car is less than 32°C (90°F) before unloading.
5. Examine all valves to be certain that they are closed before removing caps, plugs, or flanges.
6. Connect pressure supply hose to the vent valve on the tank car, and open the vent valve.
7. Connect unloading line to the eduction valve, or if bottom unloading, connect to the bottom outlet.
8. Close all bleed valves on the unloading line, and open tank car valve or valves connected to the unloading line.
9. Open pressure supply hose valve enough to keep a positive pressure on the tank car.
   Regulate the unloading gas pressure so that it does not exceed 80% of the safety valve set pressure stenciled on the side of the tank car.
10. Open unloading line valve.
11. To avoid freezing of acrylic acid in the unloading line, flow should not be interrupted.
12. When the tank car is empty, block in pressure supply hose valve, tank car unloading valve, and unloading line valve.
13. Depressure unloading line, disconnect and remove the unloading line and fittings from the tank car.
14. Vent the tank car down to minimal pressure before returning it to the shipper. If tank car cannot be depressured, add a tag stating "tank car under pressure."
15. Block in vent valve on tank car. Depressure and disconnect pressure supply hose from the car.
16. Re-install all flanges and plugs removed. Close and secure all housings. Follow DOT guidelines for securing rail car before shipment.
17. Per DOT regulations at the time of this publication, placards are **NOT** to be reversed.
18. Disconnect ground and remove wheel chocks. Remove tank car connected sign, remove derails and unlock switches.
19. Verify that tank car is empty. If tank car cannot be emptied, notify shipper before returning the tank car.

9.6 DRUMS AND INTERMEDIATE BULK CONTAINERS (TOTES)

The use of drums or IBC (totes) for transport of acrylic acid is authorized by DOT. Non-bulk performance oriented packaging standards in DOT 49 CFR178.500 require testing of non-bulk acrylic acid shipping containers for Hazard Class 8, Packing Group II. Your container supplier can perform testing and guarantee conformance to DOT requirements. Containers that may test acceptably to DOT requirements include the following:

- 55 - Gallon
  - UN 1H1, self-supporting high-density polyethylene drum.
  - UN 6HA1, steel drum with polyethylene insert.

Authorized bulk containers are described in DOT regulations 49 CFR173.243. Refer to this section for complete, up-to-date bulk packaging information, including special requirements.

DOT approved containers include the following:

- IBC
  - DOT 31A, 31B or 31N

Please consult DOT Hazardous Materials Regulations as contained in 49 CFR100-180 and/or local regulations for complete, up to date specifications on packaging and placarding/labeling requirements.

Containers of acrylic acid should be labeled properly. Before transporting, storing or handling this product, the current product and labeling information and the MSDS (available from your supplier) should be obtained, read and understood. Appropriate wording should be used on the label in addition to specific wording required by law.

Place the identifying label on each package. Stencil the generic name on the package. Proper DOT shipping name is "Acrylic Acid, Inhibited." Apply the DOT "Corrosive" label to the container. Apply the DOT "Flammable Liquid" subsidiary risk label to container.

Safe thawing and prevention of contamination can be difficult with IBC (totes). If mishandled, IBC (totes) of acrylic acid have significantly worse consequences than drums because of the increased size. For these reasons, extra care should be taken in the proper handling and transportation of IBC (totes) containing acrylic acid.

9.6.1 Carrier Information

Avoid sources of heat, sparks, or flame. Ideally, acrylic acid should be shipped between 15°C and 25°C (59°F and 77°F). Shipment at ambient conditions is acceptable if the receiver practices proper thawing procedures (see 9.6.3 on thawing, below) and finds the quality acceptable. Acrylic acid freezes at 13°C (55°F). Do not load or transport bulging or distorted drums. Bulging drums may indicate polymerization. **IF POLYMERIZATION IS SUSPECTED, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300.** CHEMTREC will contact the supplier. Also see Section 6, Instability and Reactivity Hazards and Section 11 Emergency Response for more details.

9.6.2 Storage of Drums and Intermediate Bulk Containers (totes)

Acrylic acid monomer is normally inhibited with 200 ppm of MEHQ to prevent polymerization. **AVOID FREEZING,** since the inhibitor preferentially concentrates in the remaining liquid.

The three most important considerations in shipping and handling acrylic acid are to **AVOID EXPOSURE TO ELEVATED TEMPERATURES, AVOID CONTAMINATION AND USE AN OXYGEN CONTAINING BLANKET GAS.**

- Ideally, acrylic acid should be kept between 15°C and 25°C (59°F and 77°F). Do not store in direct sunlight.
- Contamination can cause an uncontrolled polymerization which may result in violent rupture of the container, fire, serious damage to the surroundings and significant environmental impact.
- The presence of oxygen is required for the inhibitor (MEHQ) to be effective. Lack of oxygen can cause an uncontrolled polymerization.

Reuse drums or IBC (totes) only if thoroughly cleaned or in dedicated service.

Steel drums or IBC (totes) with liners should be inspected periodically. Migration or penetration of acrylic acid vapors through the liner may cause corrosion of the steel shell and leakage can occur.

Please see Section 6 for additional information on instability and reactivity hazards.

9.6.3 Thawing

NEVER USE STEAM OR ELECTRICAL HEATING IN DIRECT CONTACT WITH DRUMS OR IBC (TOTES) OF ACRYLIC ACID AS THIS CAN RESULT IN UNCONTROLLED POLYMERIZATION.

NEVER WITHDRAW MATERIAL FROM A PARTIALLY THAWED DRUM OR IBC (TOTE) OF ACRYLIC ACID. SUCH MATERIAL MAY BE UNINHIBITED OR IT MAY CONTAIN MOST OF THE INHIBITOR REQUIRED FOR THE ENTIRE CONTENTS OF THE DRUM OR IBC (TOTE).

Preferably, drums and IBC (totes) should be thawed in a heated room at a temperature between 20°C and 33°C (68°F and 91°F). This will allow the acid to thaw gradually over a 48 hour period. Each container should be agitated periodically to mix the inhibitor and dissolved oxygen during thawing (i.e. drum roller, tote agitator, pallet shaker).

When the material has thawed, the temperature of the drums or IBC (totes) should be maintained between 15°C and 25°C (59°F and 77°F).

Thawing of frozen acrylic acid can be extremely hazardous if proper procedures are not followed. When freezing occurs in drums or IBC (totes), the first crystals, low in inhibitor, will form along the outer wall of the container. Acrylic acid may be thawed by carefully applying limited heat (≤ 45°C) to the outside of a drum or IBC/tote (polymerization of the low-inhibited monomer along the walls is easily initiated).

9.6.4 Handling Procedures

Acrylic acid is a corrosive liquid and should be handled accordingly. The contents of the drums and IBC (totes) should be ***positively identified*** before it is transferred. The procedures outlined below are suggested to reduce the risks during the handling of acrylic acid.

9.6.4.1 Receipt of Drums and Intermediate Bulk Containers (totes)

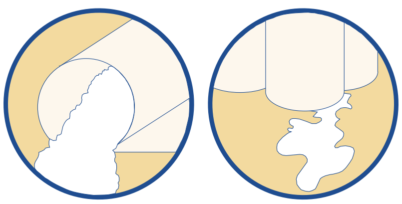
Acrylic acid is shipped in steel drums and IBC (totes) with polyethylene liners or self-supporting high density polyethylene drums and IBC (totes). When a carload or truckload of drums or IBC (totes) is received, leave the doors of the car or truck open for ventilation before entering. A persistent strong odor may indicate a leaky container.

If there is no "sloshing" noise when the drums or IBC (totes) are agitated, the material may be frozen. See Section 9.6.3 for safe thawing procedures.

9.6.4.2 Emptying of Drums and Intermediate Bulk Containers (totes)

The following steps outline procedures for safely emptying drums and IBC (totes). Refer to the ICSHAM pamphlet "Transportation of Acrylic Acid in Drums" for more information.

1. Drums and IBC (totes) must be electrically grounded during transfer operations and a static-free dip pipe or flexible stainless steel hose used to drain the acrylic acid.
2. Drums, IBC (totes) and fittings should never be struck with tools or other hard objects which may cause sparking.
3. Before removing plugs from acrylic acid drums or IBC (totes), locate the nearest emergency safety shower and eye wash station and put on personal protective equipment.
4. The preferred safe method for emptying drums and IBC (totes) is by pumping. If drums or IBC (totes) are emptied by gravity, the valves should be self-closing. Do not use pressure to displace drums or IBC (tote) contents.
5. Provide adequate vacuum breaking to prevent collapse of the drums or IBC (totes) during emptying.



10 ENVIRONMENTAL CONSIDERATIONS FOR ACRYLIC ACID

10.1 ENVIRONMENTAL FATE

Because of its reactivity, acrylic acid is generally not persistent in the environment. It disperses via a combination of mechanisms, including biodegradation, oxidation, and volatilization.

10.1.1 Biodegradation

In biochemical oxygen demand (BOD) studies, acrylic acid has been shown to degrade 81% in 22 days in water inoculated with sewage seed. Acrylic acid is also amenable to anaerobic treatment, degrading to about 75% of theoretical methane in acclimated cultures.

Acrylic acid is moderately toxic to aquatic life, but not persistent in aquatic environments, due to rapid oxidation. Large releases can deplete dissolved oxygen.

10.1.2 Volatilization / Soil Adsorption

Acrylic acid is essentially nonvolatile, although some vaporization from surface and dry soils may occur. Acrylic acid released to the atmosphere will react with ozone and photochemically produce hydroxyl radicals, resulting in a half-life of six to fourteen hours.

Since acrylic acid is miscible with water, it would not be expected to absorb significantly on soil or sediment.

10.2 DISCHARGES

10.2.1 General Information

A variety of federal, state and local regulations govern the release of any material to the land, air or surface waters. Any release or discharge of acrylic acid must be evaluated in reference to these regulations to determine appropriate response actions and reporting requirements.

A regulation called Resource Conservation and Recovery Act (RCRA) must be followed if a volume of acrylic acid or material contaminated with acrylic acid is to be disposed of or discarded. Based on RCRA criteria, acrylic acid or materials contaminated with acrylic acid will likely be considered a "Hazardous Waste" upon disposal and will need to follow certain storage, handling and disposal restrictions as outlined in RCRA. Strict adherence to these restrictions as well as proper characterization and labeling of the material is the responsibility of the generator and handler of the waste material.

Many industries are subject to the Toxic Release Inventory requirements under EPA's SARA 313 (Emergency Planning and Community Right-To-Know) regulations. Acrylic acid is one of the chemicals for which releases to all environmental media must be annually reported.

Acrylic acid is also subject to the Hazardous Substance inventory and hazard classification requirement of EPA's SARA 311 and 312 programs. Acrylic acid meets the following characteristic categories for these programs: fire, reactive, acute health, and chronic health.

10.2.2 Discharges to Navigable Waters

Discharges to streams and other navigable waters are controlled under federal and state regulations, including a National Pollutant Discharge Elimination System (NPDES). Both point-source (pipe and treatment point) and non-point-source (storm water) discharges may require permitting activities and will be required to meet site-specific effluent limitations. Non-compliance with these limitations or discharge without an effluent permit is subject to significant civil and criminal penalties.

10.2.3 Discharges to Municipal Sewers

Discharges to public sewers and treatment works are regulated by federal, state and local regulations (including effluent limitations and any pre-treatment requirements), and by the specific permit conditions for the receiving treatment works. No acrylic acid should be discharged to a municipal sewer without the prior agreement of the operator of the treatment works.

10.2.4 Emissions to Air

Discharges of chemicals into the atmosphere are generally subject to restrictions imposed by federal, state and local standards. Industrial sources of discharge of such regulated chemicals and processes are controlled by the Federal Government for both new and modified sources under a variety of laws and regulations. State regulations also control pollutants to the extent necessary to achieve or maintain national air quality standards. State and local standards may also apply to any corrosive, irritating, flammable, odorous, or other nuisance air emissions, regardless of the source. Generally, no release of acrylic acid as an air emission will be allowed without a permit from either the federal or state agencies. Non-compliance is subject to significant civil and criminal penalties.

Air pollution control devices used to remove pollutants from gaseous discharges are also often required to meet Federal, State and local standards, including regulations on the disposal of wastes from the control devices (such as scrubber water or incinerator ash).

10.2.5 Releases to Land

Treatment and disposal of acrylic acid and mixtures containing acrylic acid are subject to federal regulations and state delegation of such regulation. Acrylic acid or mixtures of acrylic acid cannot be disposed of on the land without permitting activities and without prior treatment to specific standards (see Section 10.4).

10.3 SPILL AND LEAK CONTROL

10.3.1 General Information

Emphasis should be placed on the prevention of releases through careful design of equipment and sound operating procedures. If acrylic acid is lost from containment through a leak or spill, care should be taken to use the proper personal protective equipment (see Section 5.5) decontamination procedures, and other safety considerations.

It is important to remember that spills of acrylic acid and materials contaminated by acrylic acid must be handled as RCRA hazardous wastes.

Any release of acrylic acid greater than the "reportable quantity" designated by the EPA in CERCLA or SARA should be reported immediately on discovery to the National Response Center and State Emergency Response Agency (see current MSDS for reportable quantity and pertinent phone numbers).

10.3.2 Small Spills (Up To 4 Liters)

Use proper personal protective equipment (see Section 5.5). Commercially available spill cleanup kits may be used. If biological wastewater treatment is available, or the wastewater treatment system is capable of handling the material, the spill may be sparingly diluted with water and allowed to enter the treatment system. Otherwise, use a non-combustible adsorbent to pick up the spill. Dispose of the contaminated adsorbent, any contaminated soil, and any supplies or personal protective equipment which cannot be decontaminated as RCRA hazardous waste.

10.3.3 Large Spills (Greater Than 4 Liters)

Use proper personal protective equipment (see Section 5.5). If possible, contain the spill within a diked area and recover the material in appropriate containers. Waste acrylic acid monomer may polymerize, creating additional hazards (see Section 6). Care should be taken to avoid mixing acrylic acid with incompatible materials, as noted in Section 6.1 and in the appendix on Incompatible Materials (Section 13.1). Avoid run-off into storm sewers, ditches, and other routes to surface waters. Depending on the applicable regulations and the capabilities of the receiving treatment works, the spill can be neutralized with mild alkaline chemicals, then sparingly washed down with water to the treatment system. Check with the operator of the treatment works prior to doing so.

In the event of accidental spillage of acrylic acid to surface waters or to a municipal water system, contact the local and state pollution control agencies immediately.

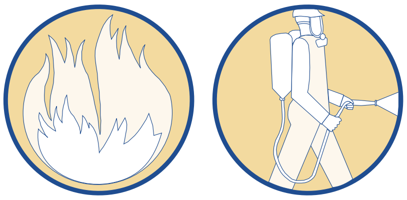
10.4 DISPOSAL OF WASTES

Acrylic acid is highly corrosive and should be handled with appropriate safety and personal protective equipment.

Acrylic acid may be diluted with water and successfully treated in an aerobic biological treatment system. However, it can be toxic to the treatment bacteria if it is introduced without any acclimation. If a significant amount of acrylic acid is to be fed to the system, special attention should be given to introducing the acrylic acid stream at low feed rates, with stepwise increases, to acclimate the system.

Acrylic acid is readily burnt in commercial incinerators and thermal oxidizer systems. Polymerized acrylic acid may also be incinerated by firms capable of handling solid waste materials.

Waste acrylic acid or materials contaminated with acrylic acid should not be landfilled. Federal and state regulations prohibit landfill of such materials without prior treatment. Local regulations and disposal site permits should also be consulted. Waste acrylic acid monomer may polymerize, creating additional hazards (see Section 6). Care should be taken to avoid mixing acrylic acid with incompatible materials, as noted in Section 6.1 and in the appendix on Incompatible Materials (Section 13.1).



11 EMERGENCY RESPONSE

Signs of an emergency involving acrylic acid often involves increased temperatures (due to external heating or a polymerization exotherm), venting of the container or container defamation. The proper initial action if there is an emergency during transport or in a user's tank or drums is to call CHEMTREC at 800-424-9300. CHEMTREC will notify the supplier and facilitate the establishment of communications between the personnel at the emergency site and the supplier's emergency response team.

Users of acrylic acid should develop written emergency plans for acrylic acid spills, fires, exotherms and incipient polymerizations. These plans should focus on clearly identifying the features that categorize an event as an emergency, what should be done to secure the emergency site and immediate actions to mitigate the danger. A very important feature of the plan should be ***early*** notification of CHEMTREC of the incident so that the supplier can quickly provide expertise in helping to manage the incident.

11.1 DETECTION AND RESPONSE TO INCIPIENT POLYMERIZATION IN A STORAGE TANK

If a system is installed and operated with all of the prevention measures recommended in this brochure and required by prudent engineering practice, the chances of experiencing an inadvertent polymerization are minimized. However, in the case of unforeseen events which might lead to incipient polymerization in a storage tank, it is necessary to detect such an event in a timely manner to avoid, stop or mitigate polymerization. An option to provide additional protection from these unforeseen events is the use of a restabilization (shortstop) system. This subsection deals with the design and operation of such an optional restabilization system.

11.1.1 Credible Initiation Scenarios

The only quantitatively definable scenarios studied kinetically for incipient runaway acrylic acid polymerizations involve external heating of the acrylic acid[30]. Two other possible causes of acrylic acid runaways are removal of the dissolved oxygen from the monomer and chemical contamination. If the monomer is purged with an inert gas (e.g., nitrogen or fuel gas) and the dissolved oxygen is removed, the MEHQ inhibitor becomes ineffective and polymerization will ultimately occur. The length of the induction period until polymerization occurs and the maximum rate of polymerization are unpredictable because they depend on the previous storage history of the acrylic acid. If inert purging is known to have occurred, the acrylic acid should be sparged with a gas containing 5 to 21 vol. % of oxygen as soon as possible. Air is preferred.

The scope of a contamination scenario is very difficult to pre-define since the identity and concentration of the contaminant are unpredictable. However, it is recommended that the restabilization (shortstop) system be immediately activated if contamination with a known or potential polymerization initiator has taken place. If such contamination has occurred without the knowledge of responsible personnel, the restabilization (shortstop) system should ultimately be activated in the event of a polymerization exotherm.

11.1.2 Polymerization Detection

The most reliable way to detect the approach to a runaway polymerization is by redundant temperature monitoring of the tank contents. This is best done by comparison of the actual temperature to the target storage temperature range, 15 to 25°C (59 to 77°F). Acrylic acid polymerization is a highly exothermic reaction (-77.5 kJ/g mole /-18.5 kcal/g mole). Due to this release of energy, polymerization in a storage tank results in heating of the liquid. A temperature monitoring system should be capable of determining not only the absolute temperature of the liquid but also the rate of rise of that temperature, whether from external heating or from a polymerization exotherm. The use of high temperature alarms to warn of overheating in the tank is necessary in acrylic acid storage. Cloudiness or turbidity may be another indication of polymerization.

11.1.3 Restabilization (Shortstopping)

Successful restabilization of acrylic acid requires a timely response to detection of a significant temperature increase. The lack of a timely response may result in the onset of polymerization leading to accelerated temperature and pressure rises. The quantitative relationships between rate of temperature rise, instantaneous temperature, and the time remaining until runaway occurs (for **thermal** initiation) have been correlated in kinetic studies[30]. These results lead to the restabilization system activation criteria given in 11.1.3.3. Due to the large number of possible contaminants and concentrations of those contaminants, these criteria **MAY NOT** apply if the cause of the polymerization is contamination.

11.1.3.1 Restabilization (Shortstop) Inhibitor

Experimental evidence leads to the recommendation of phenothiazine (PTZ) as the preferred shortstop agent. Any other materials (including MEHQ) used in this service may be ineffective or even detrimental. Phenothiazine is a solid, and for ease of mixing and addition, it should be added as a solution. While addition of PTZ has worked in most cases, there is no assurance that it will always be effective. Obvious exceptions are contamination of acrylic acid with gross amounts of a polymerization initiator or a delay in activation of the shortstop system.

Addition of a large amount of water to acrylic acid undergoing polymerization will moderate the reaction by removing heat. However, the release of large volumes of steam and acrylic acid vapor, and the possibility of tank overflow detract from this option[32].

11.1.3.2 Restabilization (Shortstop) Inhibitor Solvent

The following criteria are recommended for the selection of a solvent for the PTZ shortstop inhibitor:

- It should be a good solvent for PTZ (preferably at least 6 wt % PTZ solubility at the lowest anticipated ambient temperature).
- It should not be viscous.
- It should not promote polymerization and should be inert to the system.
- It should not be highly toxic.
- It should not exacerbate any potential fugitive emission problem resulting from the emergency.
- (Optional) If successfully shortstopped, the acrylic acid containing the solvent should be capable of being repurified.

Examples of solvents used for shortstop PTZ are ethyl acetate, isopropyl acetate, N-methylpyrrolidone and tripropylene glycol. Contact your supplier for solvent recommendations.

Ideally, one would not want to add a new chemical to the potential runaway system, so acrylic acid might be considered as a solvent for PTZ. Unfortunately, the solubility of PTZ in acrylic acid is only about 2 wt % at ambient temperature. The PTZ shortstop solution should be as highly concentrated as possible to minimize its volume so that it can be pumped into the system in as short a time as possible. The final concentration of PTZ in the acrylic acid to be shortstopped should be in the range of 200 to 1,000 ppm. However, in the case of contamination, restabilization may not be possible at any concentration of PTZ, depending on the nature and concentration of the contaminant.

11.1.3.3 Activation Criteria for Restabilization (Shortstop) Systems

It is recommended that the restabilization (shortstop) system be immediately activated if any of the following criteria is satisfied:

- A temperature rise of greater than 10°C (18°F) has been detected in one hour or less without external cause.
- The temperature in the liquid has reached 45°C (113°F).
- There is a fire near an acrylic acid tank.
- A known polymerization initiator has been inadvertently added to the acrylic acid.

These criteria have been chosen to ensure adequate time for the restabilizing agent to be fed to and dispersed in the tank contents. Lower temperatures or temperature rises than stated above may indicate an on-going polymerization. Any temperature or temperature rise that exceeds the possible rise from external heat sources (ambient, sun, pumps, temperature control systems, receipt of warmer product, etc.), may indicate an on-going polymerization. The lowest practical temperature or temperature rise should be used as a call for investigation. Manual activation of the shortstop system is preferred for sites with continuous manning; otherwise automatic activation of shortstop system should be used. In any case, the shortstop system should be activated if the criteria specified above are met.

UNDER NO CIRCUMSTANCES SHOULD ANYONE APPROACH A TANK WHOSE CONTENTS HAVE REACHED 50˚C (122˚F).

11.1.3.4 Mixing of Restabilization (Shortstop) Inhibitor

It is possible to quickly bring the concentration of the shortstop inhibitor to effective levels by circulating the tank contents with a pump[33] and/or by injecting a gas. If a pump is used to mix shortstop solution, the shutdown instrumentation must be designed to accommodate emergency procedure. The use of eductor tubes on the tank inlet(s) or a gas lift can reduce the time required to mix the shortstop solution with the tank contents.

An important factor in the design and installation of the shortstop inhibitor system is the specific tank farm layout. The number of acrylic acid tanks, the location of diked walls and the types of chemicals within the diked areas should all be considered when planning a shortstop storage and distribution system. The shortstop system should be capable of distributing adequate inhibitor to all the acrylic acid tanks which could be involved in a given incident. For multiple tank protection, the options include a single inhibitor tank with controlled metering, separate dedicated inhibitor tanks and mobile inhibitor tanks. Your supplier can provide further details.

Another consideration is the location of the inhibitor tank(s) and how their contents will be delivered to the storage tanks. If the tanks are at ground level and at some distance from the acrylic acid storage tanks, ancillary pump(s) may be necessary to transfer the PTZ solution from the inhibitor tank to the storage tank. Alternatively, the inhibitor tank(s) may be located in elevated positions near the storage tanks, with the inhibitor solution being pressured into or flowing by gravity into the storage tank's recirculation line. These options are best examined by plant personnel who will be most familiar with the specific tank farm layout.

11.1.3.5 Examples of Restabilization (Shortstop) Systems

A shortstop inhibitor system is an emergency response system for runaway polymerization mitigation in acrylic acid storage tanks. It is an optional safety enhancement. Shortstop inhibitor systems can vary in complexity and cost. The design of any such system must be based on a careful risk analysis by the user. Your acrylic acid supplier can provide further information. Figures 11-1 and 11-2 represent two examples of shortstop systems. The key to symbols in Figures 11-1 and 11-2 is found in Table 7-2.

In Figure 11-1, the inhibitor solution is 6 wt % phenothiazine (PTZ) dissolved in ethyl acetate solvent. The shortstop tank (V-2) protects acrylic acid storage tank (V-1). The tie-in of the shortstop inhibitor system with the acrylic acid tank system is at the exit of the acrylic acid tank cooler (HE-1). Rapid mixing of the shortstop inhibitor solution with the acrylic acid in the storage tank is achieved by eductor tubes inside the acrylic acid tank. The eductor tubes are located at the discharge of the acrylic acid tank pump circulation loop.

The delivery of shortstop inhibitor solution to the acrylic acid tank is based on the blowcase operation concept. The inhibitor solution is pressurized into the tank by nitrogen, air or an air/nitrogen mixture. In this example, nitrogen is chosen as the primary inert gas supply source. The air/nitrogen mixture is used as a back-up source if the nitrogen system fails. The acceptability of nitrogen in this service is based on the fact that PTZ does not require that the acrylic acid have dissolved oxygen in order to be an effective inhibitor.

After charging the shortstop inhibitor solution to the inhibitor tank, the inhibitor tank is pressurized to a suitable supply pressure. When the shortstop inhibitor system is not in service, the inhibitor tank pressure may vary as inert gas supply pressure valves leak or ambient temperature changes. Pressure changes in the tank may result in a loss of ethyl acetate by evaporation, which will increase the PTZ concentration. A PTZ concentration change from 6% to 7% will cause a PTZ crystallization point rise from about -18℃ to -9℃ (0℉ to 16℉). Therefore, when the shortstop inhibitor system is not in service, both the inert gas supply lines and the inhibitor solution tank should be isolated to minimize solvent loss.

The PTZ concentration in the shortstop solution should be checked periodically (by gas or high performance liquid chromatography [GC or HPLC], and ***NOT*** by a colorimetric method). The lower part of the inhibitor tank piping should also be checked for solid sediment (PTZ decomposition products) which might block the lines.

In Figure 11-2, the inhibitor solution is 50 wt % PTZ dissolved in N-methylpyrrolidone[35]. The shortstop tank and compressed gas cylinder can be a mobile or a fixed unit. The tie-in is made so that inhibitor solution and subsequent gas can be injected into the bottom section of the acrylic acid tank. The general steps for restabilizing an acrylic acid tank using the system illustrated in Figure 11-2 are as follows:

- Connect the shortstop tank to the delivery system with dry disconnect fittings.
- Open the appropriate automatic and/or manual valves to pressure the inhibitor solution into the acrylic acid tank using air or nitrogen (air is used in this example).
- After the shortstop tank is empty of inhibitor solution, the air will flow through the submerged nozzle at a moderate rate, mixing the contents by the gas lift principle. The air flow rate is limited by an orifice located between the air cylinder and the pressure regulator.

Contact your supplier for further information on shortstop systems.

Figure 11-1: Acrylic Acid Shortstop System Example I

This example illustrate some safety features discussed in this booklet. Not all equipment or instrumentation required for operability is shown. See Table 7-2 for key to symbols.

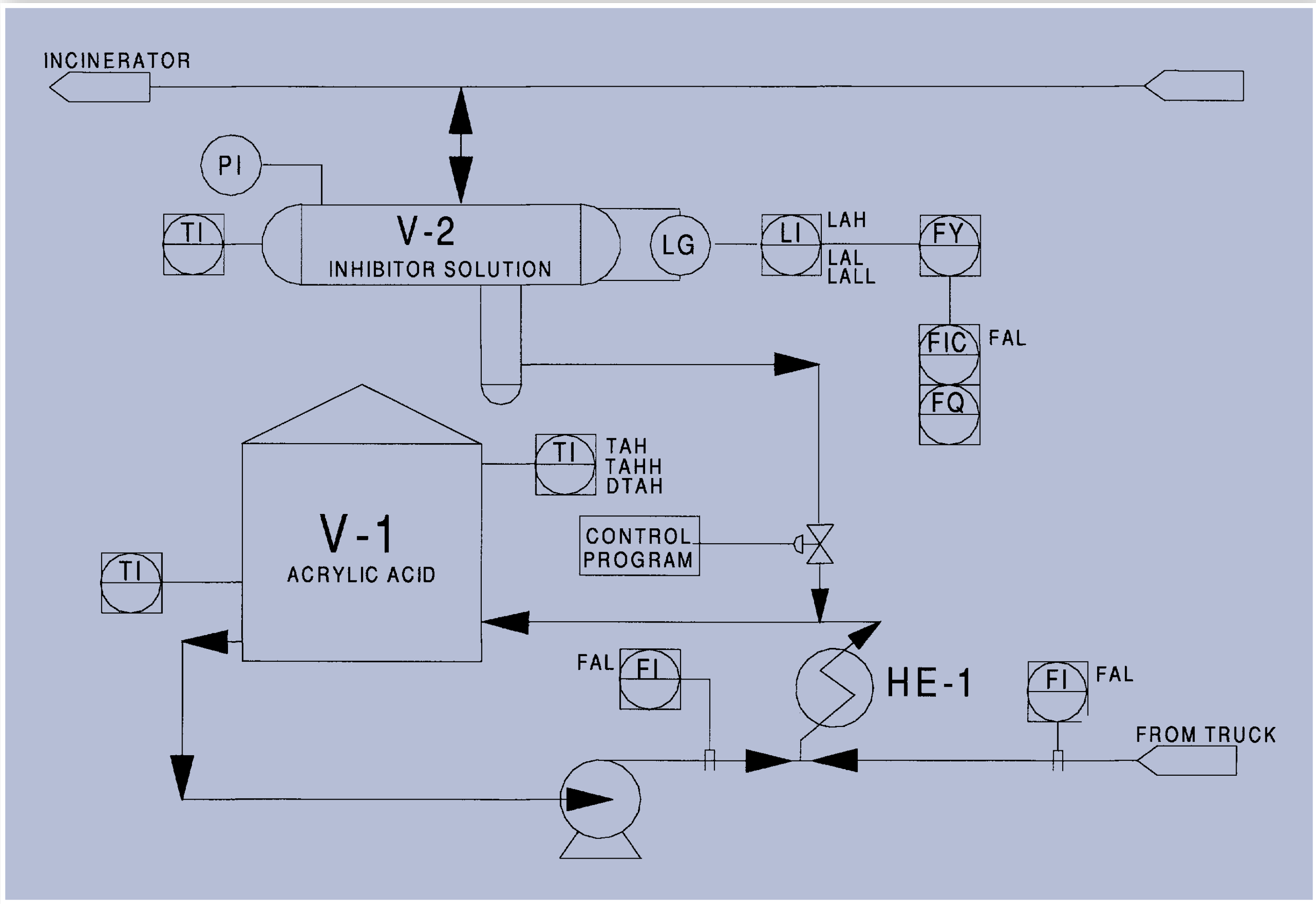
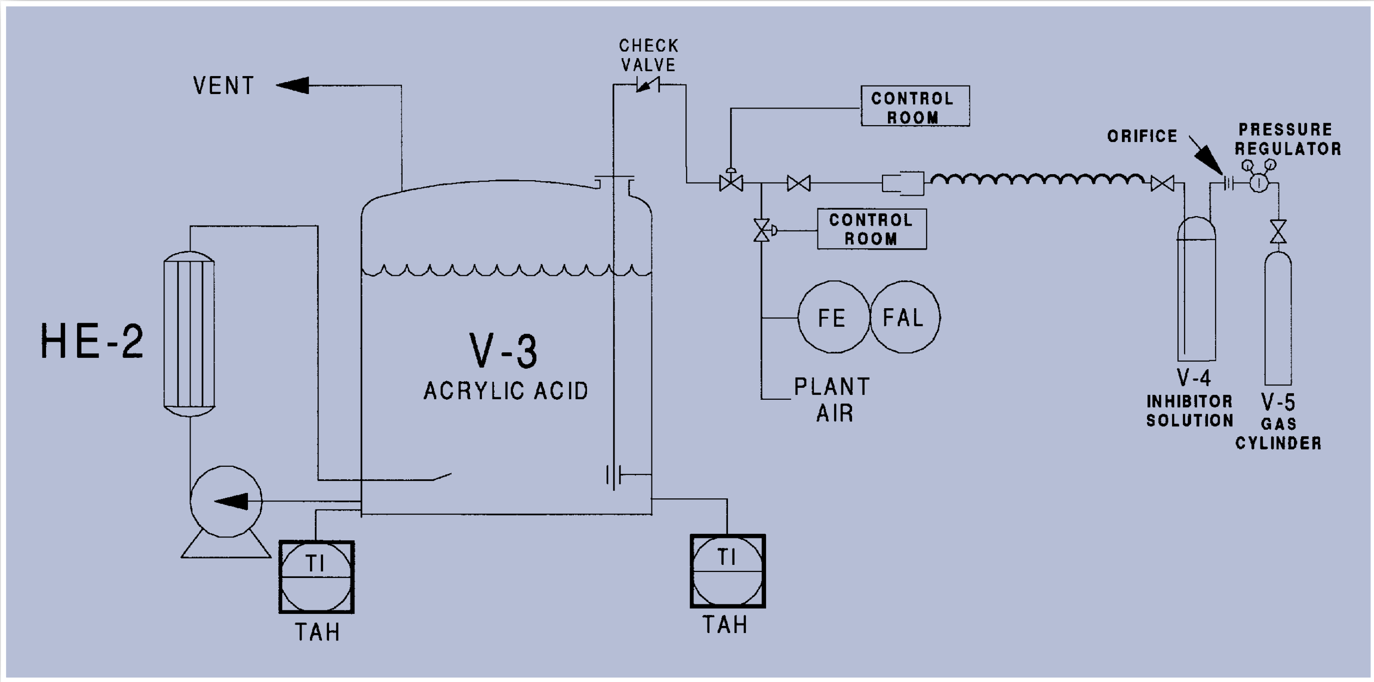


Figure 11-2: Acrylic Acid Shortstop System Example II

This example illustrate some of the safety features discussed in this booklet. Not all equipment or instrumentation required for operability is shown. See Table 7-2 for key to symbols.



11.2 SPILLS

Containment is the most important technique for handling spills. Numerous techniques have been used successfully in containing spills: for material on the ground, diking, diverting and absorption; for material still in the leaking container, plugging, patching, repairing, tightening of container fittings or secondary containment (drums).

More information on spills is given in Section 10.3.

11.3 FIRES

Acrylic acid is a combustible liquid with a flash point of 50°C (122°F). Under normal recommended storage conditions (15 to 25°C) acrylic acid is not a significant fire risk because the liquid's temperature is well below its flash point. However, acrylic acid is a reactive material which can polymerize if exposed to high temperatures. Therefore it is critical that any emergency plan contain measures to closely monitor the temperature of acrylic acid storage tanks in fire situations and be prepared to provide cooling to the storage tank if warranted. Incident commanders, fire fighters, and emergency response personnel must be trained on the polymerization hazards of acrylic acid in order to determine the proper response in an emergency.

An acrylic acid storage tank fire or a fire in the vicinity of an acrylic acid storage tank is a very dangerous situation. If the acrylic acid reaches elevated temperatures the liquid could polymerize which could result in a violent reaction, evolving considerable heat and pressure and ejecting hot vapor and polymer. Therefore it is necessary to closely monitor the temperature of the acid during a fire situation. Quick response is essential for controlling and preventing escalation of the situation.

In the event of a severe fire with or near acrylic acid, when the liquid temperature reaches 50°C (122°F) it is necessary to evacuate all non-essential personnel to a safe distance from the tank because of the risk of a runaway polymerization. At 60°C (140°F) **ALL** personnel should be evacuated.

In the event of a fire in the immediate vicinity of an acrylic acid storage tank, apply water spray or fog to the tank surface to absorb heat and maintain a lower temperature. Since many acrylic acid tanks are insulated, caution is necessary when directing a spray onto insulated tanks so as not to destroy the insulating material. If a tank has a cooling system, verify that the cooling system is turned on and operating at maximum capacity. Keep a close watch on the temperature of the storage tank. If the temperature of the acid is rising despite the application of cooling water and the cooling provided by the cooling system, it may be necessary to add a shortstopping agent. If the temperature of the acid equals or exceeds 45°C (113°F), then a shortstopping agent should be added to limit the risks of acrylic acid polymerizing and escalating the situation. Shortstopping agents can be injected using one of the systems outlined in Section 11.1.3.6 of this manual. Please note that shortstopping systems are optional and each facility must evaluate its risks associated with handling and storing acrylic acid and determine the necessity for a shortstopping system.

In the event that the acrylic acid tank has caught fire, the first step should be to add a shortstop agent as quickly as possible. This will help to prevent a runaway polymerization from occurring, assuming that this was not the cause of the fire. Alcohol resistant fire fighting foam can be used to control or extinguish the fire. If foam is unavailable, water can also be used to extinguish the fire. *Please note* that water and/or foam should not be added into a tank of burning acrylic acid if the temperature of the liquid in the storage tank has exceeded the boiling point of water 100°C (212°F). This is because the water could be rapidly vaporized, causing a significant pressure surge and massive venting of a mixture of steam containing acrylic acid vapor.

Consult NFPA 11 for the proper design of fire fighting foam systems. After the fire, continue to monitor the temperature of the storage tank for at least 48 hours to verify that the temperature is not rising and the tank is stabilized.

12 ACKNOWLEDGMENTS

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13 APPENDIX

13.1 INCOMPATIBLE MATERIALS

Almost any contamination can potentially destabilize the monomer and should be avoided. The following is a partial list of chemicals which are considered to be incompatible with acrylic acid. In most cases, these contaminants cause polymerization of the monomer.

1. peroxide or peroxy- in name
2. per in name, e.g., t-butyl**per**acetate
3. peresters or peroxyesters
4. percarbonates or peroxycarbonates
5. hydroperoxide or hydroperoxy- in name
6. azo compounds
7. azides
8. ethers
9. amines
10. conjugated polyunsaturated acids and esters
11. aldehydes and some ketones
12. reactive inorganic halides (e.g. thionyl chloride, sulfuryl chloride)
13. caustics (e.g., NaOH, KOH, $Ca(OH)_2$)
14. strong mineral acids (e.g., nitric, sulfuric, hydrochloric acids)
15. oxidizing agents (e.g., chromic acid, permanganates, nitric acid)
16. varnish
17. inert gases (< 5% vol. % oxygen)

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ELF ATOCHEM NORTH AMERICA, INC. 2000 Market Street Philadelphia, Pennsylvania 19103 (215)419-7000	**ATONA**	**1/00/300**
ROHM AND HAAS COMPANY 100 Independence Mall West Philadelphia, Pennsylvania 19106-2399 (215)592-3000	**R&H 84C16**	**1/00/500**
UNION CARBIDE 39 Old Ridgebury Road Danbury, Connecticut 06817-0001 (203)794-2000		**1/00/100**