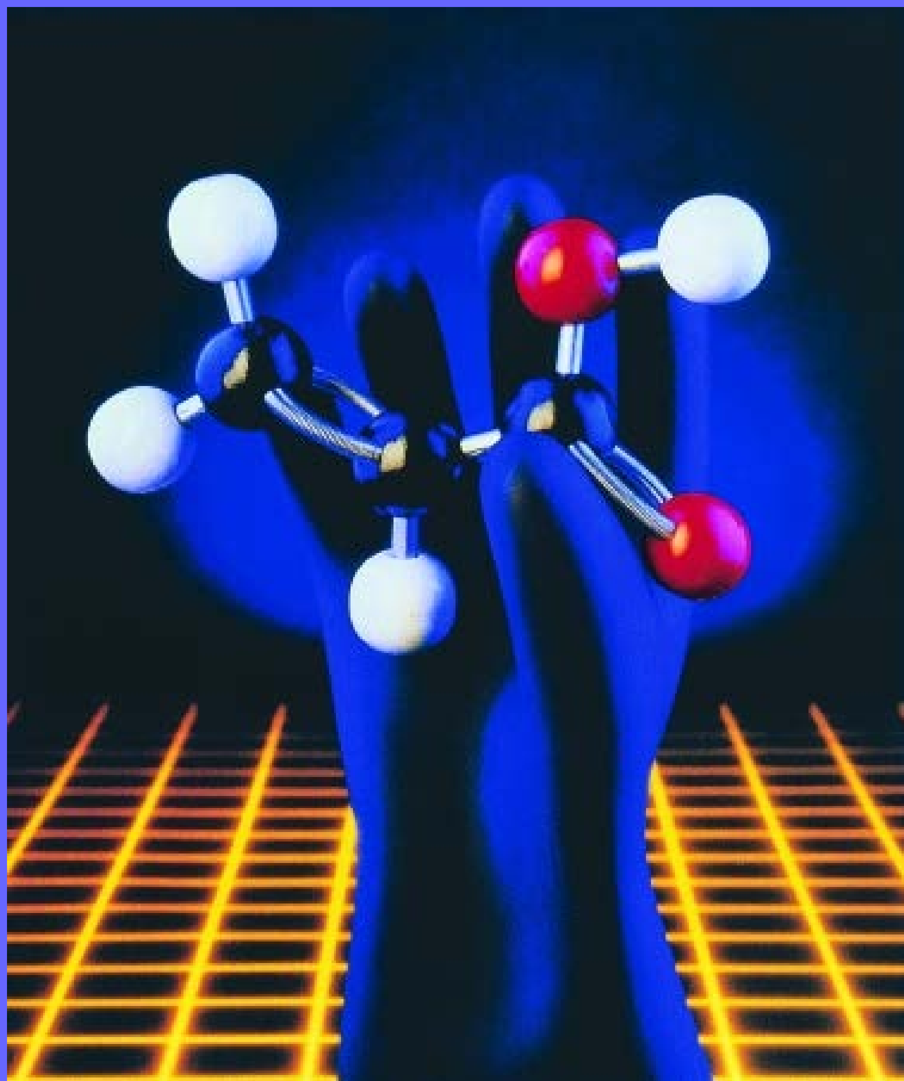
# Acrylic Acid

A Summary of Safety and Handling 4th Edition 2013



*Compiled by*
**Basic Acrylic Monomer Manufacturers, Inc.**

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## ACKNOWLEDGEMENTS


Grateful appreciation is given to the expertise of each participating company for compiling the information presented in this publication.

# 1 INTRODUCTION

The Basic Acrylic Monomer Manufacturers (BAMM), Product Stewardship Committee, formerly 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. This group is committed to sharing information on the safe handling and storage of acrylic monomers among themselves and with their customers, carriers and other handlers of acrylic monomers. The member companies are Arkema Inc., BASF Corporation, and The Dow Chemical Company.

The purpose of this brochure is to provide general information on the safe handling and storage of acrylic acid inhibited with hydroquinone monomethyl ether (MEHQ, methoxyphenol), hereafter referred to as acrylic acid. (Commercial acrylic acid also is known as glacial acrylic acid, or GAA.) The information in this brochure is based on research and experience of participating companies in addition to information taken from credible 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. Even when properly inhibited, polymerization can be caused by contamination or excessive heat. 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 35 years. In several cases, explosions caused by excessive or inadvertent heating of a container 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, redundant temperature monitoring, recirculation of the acrylic acid through a tempered water 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.

**ALTHOUGH THIS DOCUMENT REPRESENTS AN OVERVIEW OF PRACTICES USED BY NORTH AMERICAN MANUFACTURERS OF ACRYLIC ACID, IN SOME CASES THE PRACTICES OF INDIVIDUAL PRODUCERS MAY BE MORE STRINGENT THAN THE GUIDANCE OFFERED IN THIS SUMMARY. IT IS RECOMMENDED THAT USERS OF ACRYLIC ACID, IN DEVELOPING PROCESSES AND PRACTICES FOR HANDLING ACRYLIC ACID, REVIEW INDIVIDUAL PRACTICES DIRECTLY WITH THEIR SUPPLIERS. BAMM AND ITS MEMBER COMPANIES BELIEVE THE INFORMATION CONTAINED IN THIS DOCUMENT IS FACTUAL. HOWEVER, NO WARRANTY OR REPRESENTATION (INCLUDING ANY WARRANTY OF MERCHANTABILITY, FITNESS FOR A PARTICULAR USE OR NON-INFRINGEMENT OF THIRD PARTY PATENTS) EXPRESSED OR IMPLIED, IS MADE WITH RESPECT TO ANY OR ALL OF THE CONTENT HEREIN. BAMM AND ITS MEMBER COMPANIES ASSUME NO LEGAL RESPONSIBILITY FOR YOUR USE OF THIS INFORMATION AND URGE YOU TO MAKE ALL APPROPRIATE INVESTIGATIONS AND TESTS TO DETERMINE THE APPLICABILITY OF THIS INFORMATION TO YOUR SPECIFIC SITUATION. ANY MENTION OF A BRAND NAME IS FOR EXAMPLE PURPOSES AND IS NOT INTENDED TO INDICATE ENDORSEMENT OR SPECIFIC USE BY ANY COMPANY.**

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## 2 NAME AND GENERAL INFORMATION

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

| | |
|---|---|
| Chemical Name | Acrylic Acid |
| Common Name | Acrylic Acid |
| Synonyms | Propenoic Acid<br>Acroleic Acid<br>Vinyl Formic Acid<br>2-Propenoic Acid<br>Glacial Acrylic Acid (GAA) |
| CA Registry (CAS) Number | 79-10-7 |
| EINECS Number | 201-177-9 |
| Chemical Formula | $CH_2$=CHCOOH |
| Stoichiometric Formula | $C_3H_4O_2$ |
| United Nations Number | UN2218 |

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## 3 PROPERTIES AND CHARACTERISTICS OF ACRYLIC ACID

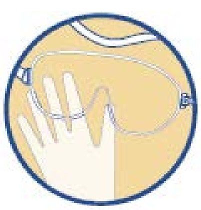
The following physical values were taken from DIPPR (Design Institute for Physical Properties) where possible. DIPPR is a subsection of AIChE (American Institute of Chemical Engineers) and specializes in compiling physical property data banks for various chemicals.

**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<br>20°C<br>30°C | <br>1.05 g/mL<br>1.04 g/mL | |
| Solubility<br>In water<br>In organic solvents | <br>Infinite<br>Freely soluble in most solvents | |
| Hygroscopicity | Is hygroscopic | |
| *Flammable Limits (% by volume in air at 760 mm Hg) | LEL 2.4<br>UEL 17 | 10, 17, 24<br>10, 18, 19 |
| Flash Point<br>Tag Closed Cup<br>Tag Open Cup | <br>50°C<br>54°C | |
| *Autoignition Temperature | 412°C | 10 |
| *Boiling Point<br>760 mm Hg<br>50 mm Hg<br>10 mm Hg | <br>141°C<br>69°C<br>40°C | 3, 13 |
| Vapor Pressure<br>20°C | <br>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<br>20°C<br>40°C<br>50°C | <br>1.19 cp<br>0.85 cp<br>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 | $5.5 \times 10^{-5}$ | 16 |
| Electrical conductivity | ~ $1 \times 10^{-3}$ µS/cm | 23 |
| *Thermal Conductivity<br>20°C<br>100°C | <br>0.159 W/m/K<br>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<br>1kHz<br>100 kHz | <br>E = 6<br>E = 8 | 23 |
| Electrical Group Classification (NEC) | ClassI 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.

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# 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). The principles of a Responsible Care Management System® should be considered.

All employees and contractors who handle acrylic acid should be thoroughly trained in the potential hazards, operating procedures, spill and leak prevention techniques, emergency response plans, personal protective equipment, and environmental protection that are relevant to their jobs. The use of an MSDS (Material Safety Data Sheet), the information in this document, and guidance from a supplier are all 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). A one page safety guide for storage and handling can be found in Appendix B.

### 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, and other information. The Glacial Acrylic Acid Audit and Assessment Protocol in Appendix E will assist your team with this process.

A typical review team utilizes expertise from operations, engineering, construction, safety, health, and environmental functions. Acrylic acid is regulated by the US EPA Risk Management Program, which requires a Process Hazard Analysis be completed by multifunctional teams. EHS (Environmental, Health and Safety) reviews should be documented and subject to the management of change process developed for your facility.

### 4.3 WRITTEN OPERATING PROCEDURES

Written operating procedures 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 as well as the actions required to reduce the risk of exposure or injury to operating personnel. It is a good practice that all responsible 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.

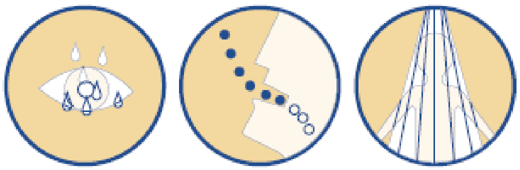
**REGULARLY HELD MEETINGS, WHICH COVER SAFETY, HEALTH, AND ENVIRONMENTAL ISSUES, ARE AN ESSENTIAL PART OF TRAINING. ALL RELATED HAZARDS, INCIDENCES, AND SUGGESTIONS SHOULD BE PERIODICALLY REVIEWED IN THESE MEETINGS AND ATTENDANCE SHOULD BE DOCUMENTED.**

### 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 will notify the supplier and facilitate the establishment of communications between the personnel at the emergency site and the supplier's emergency response team. **CHEMTREC should always be contacted if a transport vessel is involved.**



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# 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 (5.9 mg/m$^3$) 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

The greatest 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.

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

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 is designed to protect against potential adverse health effects.

## 5.2 INDUSTRIAL HYGIENE

### 5.2.1 General

Industrial hygiene involves the anticipation, 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 vapors or mist to be released. 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. Air sampling methods are available from OSHA and NIOSH (National Institute for Occupational Safety and Health) for both area and personal sample collection.

It is recommended that acrylic acid always be used in closed systems, with local exhaust ventilation, to prevent or reduce occupational exposures. When these controls are not possible, acrylic acid handling should be conducted in a well ventilated area. When other control measures are not available, impractical, or fail (e.g., 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 and acrylic acid is corrosive to all tissues. Skin contact may 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, chemical protective 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 standard operating procedures for acrylic acid handling. Non-routine events such as, spills, leaks, and other emergency situations, will create a greater potential for employee exposure. During non-routine events, there may not be time to measure acrylic acid concentrations prior to selecting protective equipment. 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. Additionally decontamination or disposal of chemical protective equipment and tools should be addressed.

## 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 so that in the event of an exposure they are immediately accessible. 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. If the person can walk they should walk out of the immediate area. Liquid acrylic acid is extremely slippery so care is necessary to prevent a fall that would increase 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. Any available person should be instructed to call for help while assistance is being provided to the affected individual. Any person assisting the exposed person must take care not to also become injured. Clothing or skin contaminated with liquid acrylic acid may secondarily contaminate rescue and medical personnel by direct contact

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. Two way communication such as hand held radios are a best practice when personnel are working with hazardous chemicals.

Immediate priorities must follow the "**A, B, C's**" of resuscitation:
**Airway** (make sure the airway is not blocked by the tongue or a foreign body)
**Breathing** (check to see if the patient is breathing, provide ventilation with use of appropriate barrier devices, e.g. with a pocket face mask, if breathing is absent)
**Circulation** (check for a pulse, initiate cardiopulmonary resuscitation if pulse is absent)

### 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 20 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 20 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 ITEMS CONTAMINATED WITH ACRYLIC ACID 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 MUST 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 medical assistance should be requested. Acrylic acid exposure usually causes mucous membrane irritation, sore throat, and coughing. Rapid development of respiratory distress with chest pain, difficulty breathing, swelling of the throat and accumulation of fluid in the lungs (shortness of breath, cyanosis, expectoration, cough) may occur. Lung injury may progress over several hours. Medical professionals or those properly trained may consider administration of oxygen.

#### *5.4.4.1 Suggestions to Physicians*

**Acrylic Acid Dose-effect Relationship from the American Industrial Hygiene Association Emergency Response Planning Guidelines (ERPG) 2010**

| Concentration | | Effects of inhalation |
|---|---|---|
| 0.1 ppm | | Odor threshold |
| 1 ppm | ERPG-1 | The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor. |
| 50 ppm | ERPG-2 | The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. |
| 250 ppm | ERPG-3 | The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects. |

In most exposures, administration of atmospheric oxygen at atmospheric pressure has been found to be adequate. Treatment should be as indicated by arterial blood gases or oximetry findings.

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. Use of a face shield, in conjunction with splash goggles, offers additional protection of the face from splashing. 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. 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. Use of a face shield, over splash goggles, offers protection of the face from splashing. 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 mm thickness or thicker 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.

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## 6 INSTABILITY AND REACTIVITY HAZARDS

### 6.1 POLYMERIZATION

Properly inhibited acrylic acid is normally stable for up to one year from the date of production when stored and handled under recommended conditions. Failure to follow recommended conditions associated with temperature, inhibitor, dissolved oxygen or contamination will significantly shorten the safe storage life of acrylic acid. Commercially available acrylic acid is stabilized (inhibited) with 180-220 ppm 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. Specific recommendations regarding temperatures are given below. Even if all the storage conditions described in this manual associated with temperature, inhibitor, dissolved oxygen, and contamination are met; acrylic acid should not remain in a shipping container for longer than one year due to peroxide build-up. **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.**

Many serious incidents involving acrylic acid have been reported. 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 include 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]. Dissolved oxygen converts carbon centered radicals to oxygen centered radicals, which the MEHQ can trap to stabilize the acrylic acid. 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. Acrylic acid being loaded into drums, rail cars, tank trucks, or other closed containers, must have a concentration of dissolved oxygen equivalent to the saturation concentration when acrylic acid is in equilibrium 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. Never use pure oxygen as it can reduce stability and increase the flammability of acrylic acid.

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. A minimum MEHQ concentration of 180 ppm is necessary **BUT NOT SOLELY SUFFICIENT** for adequate stability. Other factors influencing stability are concentration of dissolved oxygen and level of oligomeric peroxide content that accumulates as MEHQ traps oxygen centered radicals. Oligomeric peroxides accumulate over time and are reasonably stable in properly handled acrylic acid. High levels of oligomeric peroxides accumulated in overaged or improperly handled acrylic acid can break down to form additional radicals and may defeat the capability of MEHQ in such acrylic acid. Acrylic acid must be properly handled and used prior to expiration of its shelf life to prevent excess accumulation of oligomeric peroxides.

Good housekeeping and engineering must be exercised to strictly avoid contamination of acrylic acid. Many substances are known that promote its polymerization, such as peroxides and peroxide-forming compounds and free-radical-generating compounds including but not limited to hydroperoxides, aldehydes, ethers, and azo compounds. 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. Appendix A has further information on materials that are incompatible with acrylic acid.

Acrylic acid tanks should be protected from mistakenly being charged with other materials. Verification of materials prior to unloading and the use of dedicated loading and unloading lines, with proper identification, has been found effective to avoid product mix-ups. Tanks should also be protected from contamination by back flowing liquids from production vessels or by common vent systems.

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. If the chemicals added to the slop container are not monitored or controlled, 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, and recirculation of the acrylic acid through a tempered water 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 are often used, as part of an emergency response plan, 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. 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. Freezing causes all non-acrylic acid components to concentrate in the liquid phase, potentially leaving the crystalline phase severely deficient in MEHQ inhibitor and dissolved oxygen. Conditions during thawing, such as localized areas of heat, also may cause rapid polymerization.

The use of tempered water tracing and/or insulated containers is 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). Temperatures above 45°C (113°F) can lead to runaway polymerization; therefore, the temperature of the medium used to thaw acrylic acid should never be greater than 35-45°C (95-113°F).

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

- **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 electrical tracing temperature cannot exceed 35-45°C (95-113°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 ≤ 35-45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 35-45˚C (95-113°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 acrylic acid should be closely monitored and controlled.
- The acrylic acid 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 (e.g., 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. Frozen material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice.**

## 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.

CH2=CH-COOH ⇌ CH2=CH-COO$^-$ + H$^+$
*Acrylic Acid Ionization*

CH2=CH-COO$^-$ + CH2=CH-COOH ⟶ CH2=CH-COO- CH2 – $\overset{-}{\text{CH}}$ – COOH $\xrightarrow{H^+}$
*Michael-type addition*

CH2=CH-COO-CH2-CH2-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.

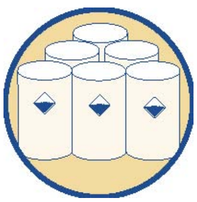
The formation of dimer is not hazardous but may affect the performance of the acrylic acid in some applications.

## 6.4 EFFECT OF WATER

Deionized water is sometimes added to acrylic acid to reduce its freezing point and / or ease its handling for some applications. Process or tap water should never be used for this purpose. Metals or minerals typically dissolved in process or tap water can substantially reduce the stability of acrylic acid and must be avoided. Even with the use of deionized water, dimerization rates increase and acrylic acid's stability is reduced significantly. Water reduces the solubility of oxygen, which is needed for inhibition. Diluted acrylic acid is less stable and deteriorates in quality much faster than undiluted acrylic acid. [37,38,39] **Acrylic acid-water solutions should be quickly consumed after preparation.** Please contact your supplier for advice if you intend to dilute your acrylic acid.

### 6.5 CORROSIVENESS

Acrylic acid is a strong corrosive to many metals like unalloyed steel (carbon steel), copper, silver and brass. Frequently the corrosive reactions with such metallic materials generate a deep discoloration in acrylic acid. Polyvalent metal salts formed during such reactions might induce polymerization. **Therefore, under no circumstances should acrylic acid be stored or transported with equipment which contains the above mentioned metals**. Acrylic acid is compatible with 304 and 316 stainless steel**.**



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## 7 BULK STORAGE FACITILIES 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 ≤ 35-45°C (95-113°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 electrical tracing temperature cannot exceed 35-45°C (95-113°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 ≤ 35-45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 35-45°C (95-113°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 minimum 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.** Such material may be uninhibited or contain most of the inhibitor required for the entire contents of the 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.**

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. See Sections 7.2.1 and 7.2.3 for further guidance.

**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.

Please see Section 11 for details associated with a shortstop system, if a shortstop system is planned for mitigating a polymerization in your storage system.

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

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 (see Section 5.1).

## 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 is 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. A complete acrylic acid audit and assessment protocol for acrylic acid storage can be found in Appendix E. Contact your acrylic acid supplier for additional guidance.

A floating roof tank is not recommended for acrylic acid storage as it creates a seal or barrier between the acrylic acid and its source of oxygen replenishment above the roof. Use of a floating roof tank for acrylic acid storage dramatically increases the likelihood of a runaway polymerization.

### 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 electrical tracing temperature cannot exceed 35-45°C (95-113°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 ≤35- 45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 35-45°C (95-113°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 below.

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.** Exceeding 32°C (90°F), even for a short time, may reduce the shelf life of the product. Investigation must include determining the cause for the abnormally high temperature and correcting that cause. Failure to correct could jeopardize the stability of the acrylic acid and necessitate emergency response (covered in Section 11). During colder months, the system can be used to avoid freezing but the heat transfer fluid must be maintained at ≤ 35-45°C (95-113°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). Cooling capacity over and above that needed to control temperature to prevent dimer formation can delay detection of temperature increases indicative of polymerization during the onset of an emergency (see Section 11).

Four commonly used temperature control systems for bulk acrylic acid tanks are given below, in order of preference:

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 (redundancy is recommended):

- A power monitor that senses 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.
- A recirculation line back to the tank, with flow indication, can provide minimum flow to avoid deadheading, but will not protect the pump from running dry (see above). Such a recirculation line must be designed to never be blocked (locked open valves if valves are needed) and able to maintain a minimum required flow through the pump even when instrumentation or valve failures occur. Orifice plate or line size can be used to limit flow to the desired minimum.
- 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). Multiple independent layers of protection are recommended**.**

Other considerations associated with pumping acrylic acid are given below:

- Double mechanical seal (requires 5 – 21% oxygen, if gas buffered) 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 at least 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 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). Temperature probes may accumulate polymer after extended use and should be included in any periodic tank inspection. 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 ≤ 30-45°C (95-113°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 electrical tracing temperature cannot exceed 35- 45°C (95-113°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 ≤ 35-45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 35-45°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 (see Section 5.1). 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 at least 110% of the entire contents of the largest tank, are suggested. New dike design is encouraged to hold at least 30 minutes of fire water flow in addition to 110% of the contents of the largest tank. The dike design must also satisfy all regulatory requirements. Spill containment for bulk unloading areas will reduce environmental risks. Concrete containment is suggested for bulk unloading areas. Storage of incompatible materials in the same containment area is not recommended. 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. Tanks or pipelines containing flammables should not be located adjacent to or within the same dike as an acrylic acid tank. If the latter is unavoidable, sprinkler systems must be well designed to protect the acrylic acid tank from the potential heat of radiation from a fire. 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 carbon steel or alloys containing copper, such as brass, or silver. 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 typically equipped with coils that can be connected to a properly designed heat transfer fluid system. The heat transfer fluid temperature should be ≤ 35-45°C (95-113°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). Never clear lines with nitrogen or steam.

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 ≤ 35-45°C (95-113°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 material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice.**

Frozen piping, valves, fitting, and pumps can be safely thawed by applying tempered water which does not exceed 35-45°C (95-113°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. When flame arrestors are used, 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 CFR 1910.106 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 Section 6.1 on Polymerization and Section 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 blanket gas containing 5-21 vol% oxygen 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 switch, which shuts off the unloading pump and / or shuts a fill valve, 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.

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**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 temperature 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 21 vol% of oxygen (dry, oil-free air is preferred) for blanketing acrylic acid storage vessels and for blowing out acrylic acid lines. Never use steam or nitrogen for blowing out 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, 7.2.11 |
| Provide engineering safeguards to reduce the risk of a violent inadvertent polymerization of acrylic acid 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

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| Feature | Section Reference |
|---|---|
| DTAH | Temperature change alarm – high |
| FAL | Flow alarm – lot |
| 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** Table of Contents

This example illustrates some of the safety features discussed in the booklet. **Not all equipment or instrumentation required for operability is shown.** Specifics of your own facility will determine details of your design. See Table 7-2 for key to symbols.

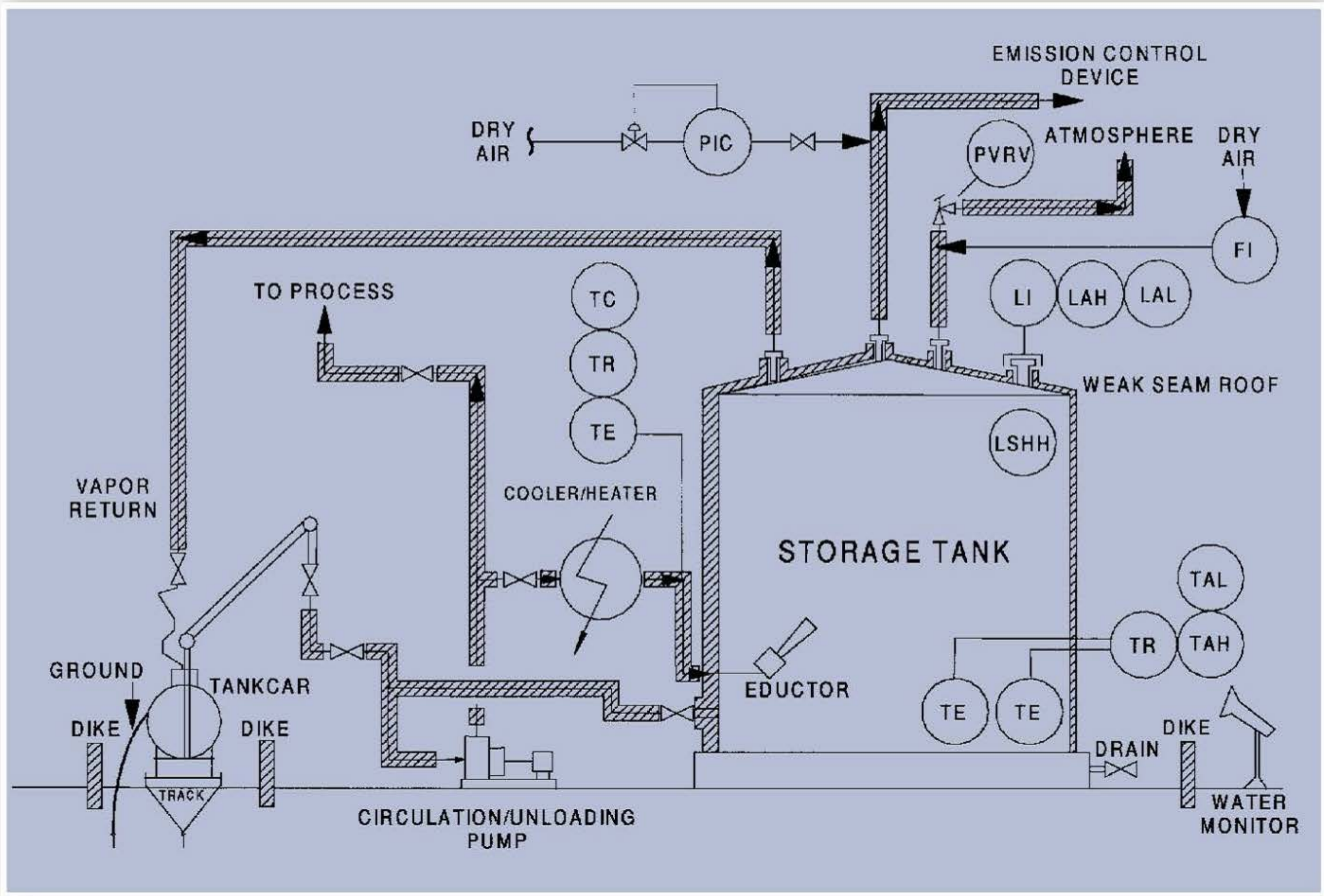


**Figure 7-2: Example of an Acrylic Acid Storage Tank Temperature Control System** Table of Contents

This example illustrates some of the safety features discussed in the booklet. **Not all equipment or instrumentation required for operability is shown.** Specifics of your own facility will determine details of your design. See Table 7-2 for key to symbols.

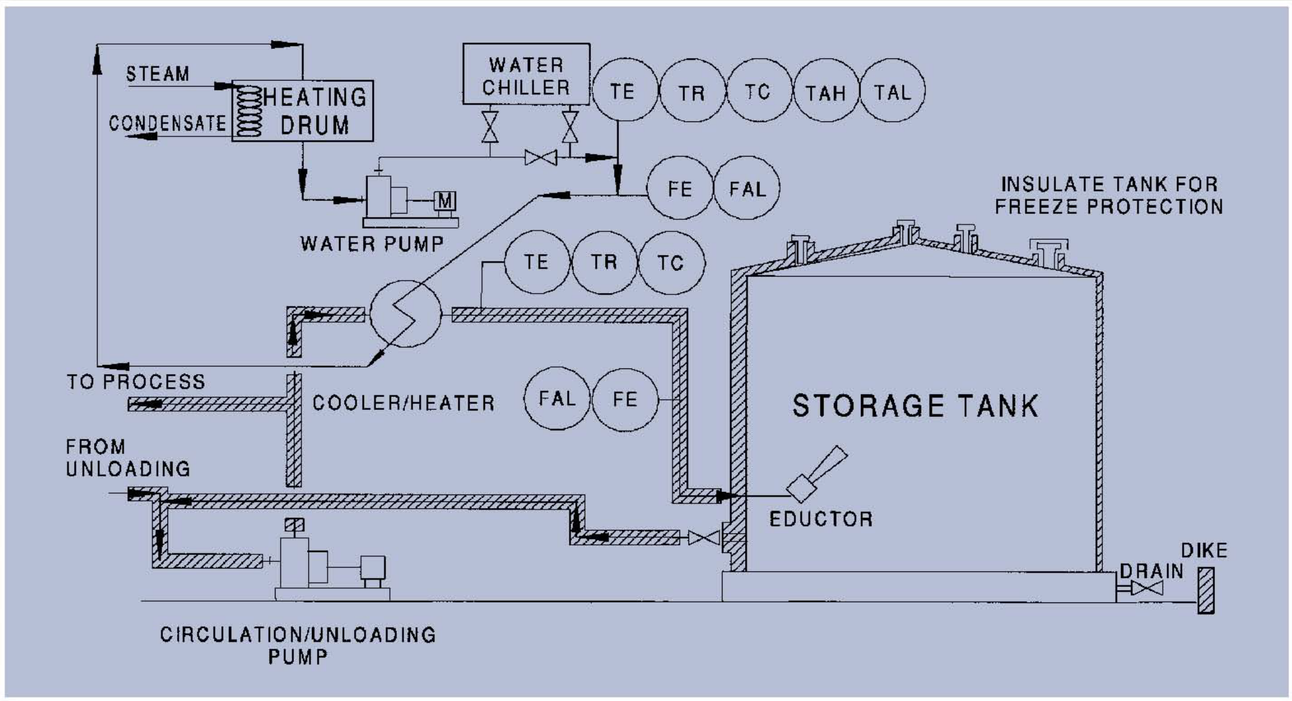
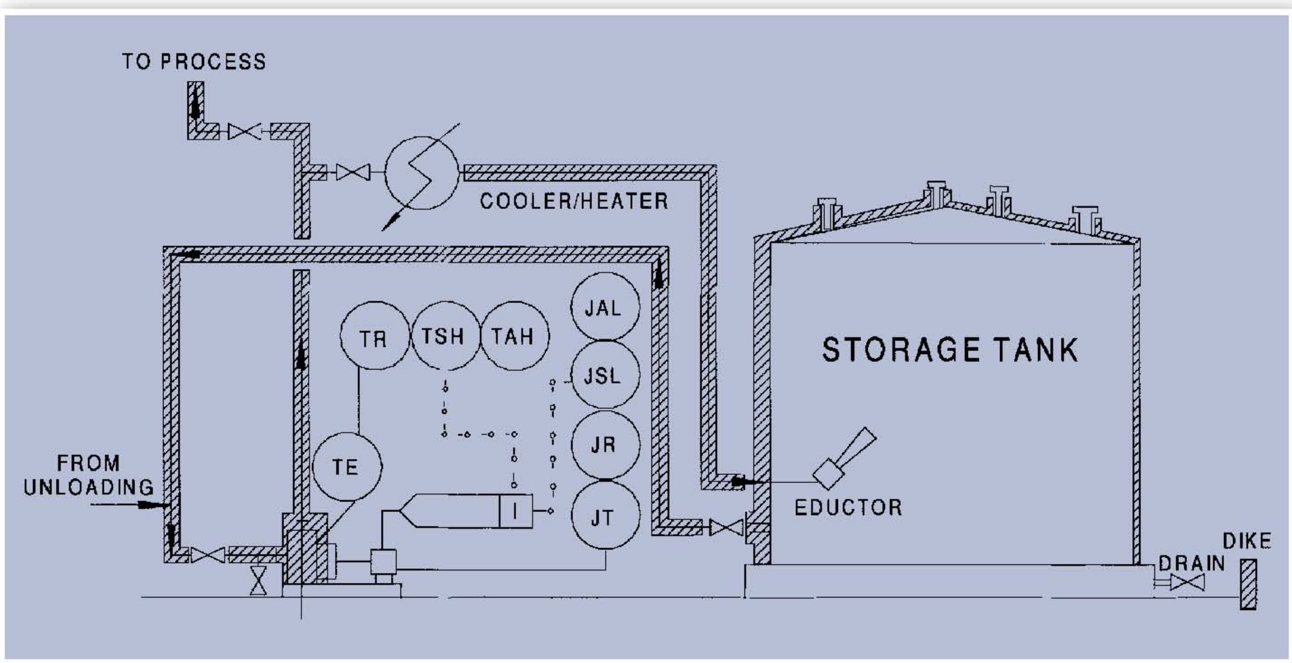
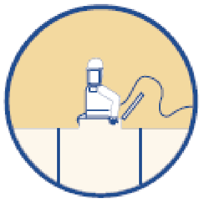



**Figure 7-3: Example of an Acrylic Acid Pump Loop** Table of Contents

This example illustrates some of the safety features discussed in the booklet. **Not all equipment or instrumentation required for operability is shown.** Specifics of your own facility will determine details of your design. See Table 7-2 for key to symbols.





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# 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 (see Appendix A). 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. Clean, dry, oil free air is preferred. Never use steam or nitrogen. 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 use steam or additional water wash 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.

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# 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. 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. See also Section 5.5.

## 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. A one page safety guide summary for the transportation of acrylic acid can be found in Appendix C.

- Acrylic acid must be stored in an oxygen-containing (5-21 vol. %) 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 steam, 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.
- Clean, dry, and oil free air or a gas mixture with 5 to 21 vol. % of oxygen is required for use in handling acrylic acid.
- Avoid incompatible materials of construction listed in Section 7.2.8.
- 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 [35-45°C (95-113°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 electrical tracing temperature cannot exceed 35-45°C (95-113°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 ≤ 35-45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 35-45°C (95-113°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 (Department of Transportation) regulations, 49 CFR Section 172.101. As such, it must be packed in DOT specification containers when shipped. The IMDG (International Maritime Dangerous Goods) classification is "Corrosive, Flammable." International shipping requirements should be reviewed to determine compatibility with United States and IMDG requirements.
- 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.** Investigation must include determining the cause for the abnormally high temperature and correcting that cause. Failure to correct could jeopardize the stability of the acrylic acid and necessitate emergency response (covered in Section 11).

- 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 and facilitate the establishment of communications between the personnel at the emergency site and the supplier's emergency response team

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 and facilitate the establishment of communications between the personnel at the emergency site and the supplier's emergency response team.

For any incident, 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, as of this writing:

- 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. Dimer formation is not a hazard, but affects the quality of the acrylic acid. **TEMPERATURES OF 32°C (90°F) OR HIGHER CAN BE HAZARDOUS AND SHOULD BE**

**IMMEDIATELY INVESTIGATED.** Investigation must include determining the cause for the abnormally high temperature and correcting that cause. Failure to correct could jeopardize the stability of the acrylic acid and necessitate emergency response (covered in Section 11). 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 35-45°C (95-113°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 and facilitate the establishment of communications between the personnel at the site and the supplier's emergency response team. 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. See Section 6 on instability and reactivity hazards and Section 11 on emergency response for more details.

### 9.4.2 Thawing Tank Trucks

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 35-45°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) in acrylic acid service unless it can be ensured that the resulting maximum electrical tracing temperature cannot exceed 35-45°C (95-113°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 ≤ 35-45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 35-45°C (95-113°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**. Frozen material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice. Such material may be either uninhibited or contain most of the inhibitor required for the entire contents of the tank truck, depending on the method used to thaw the material. 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. Dimer formation is not a hazard, but affects the quality of the acrylic acid.

### 9.4.3 Unloading Tank Trucks

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.

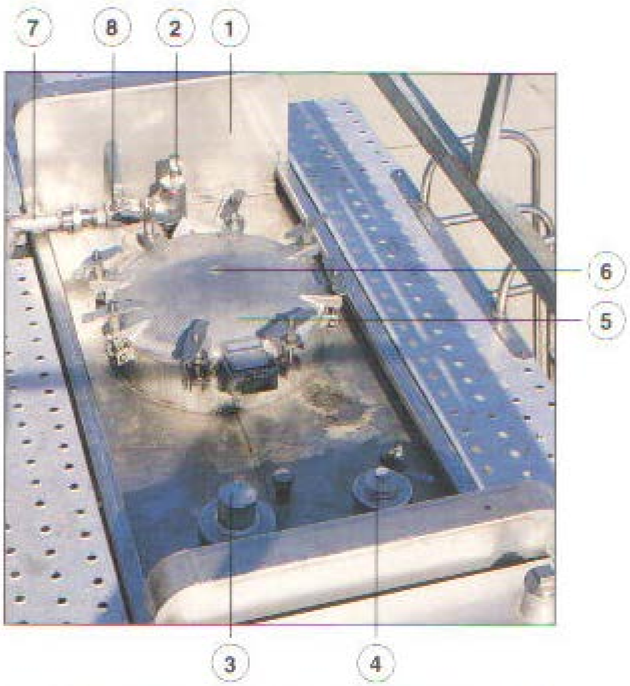
Proper equipment should be used to protect against spills. The piping for unloading should be on continuous circulation or arranged so the acrylic acid will drain toward the storage tank when transfer is stopped. Where necessary, a check valve should be provided on the unloading hose to ensure that total storage 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.

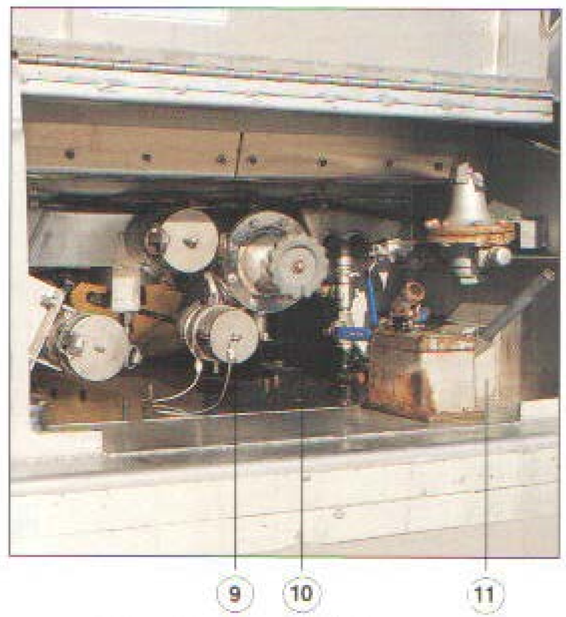
#### *9.4.3.1 Pumping Trucks with Closed Loop System*

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) and above the freezing point of acrylic acid, 13°C (55°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 (77°F).
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.

**FIGURE 9-1: ACRYLIC ACID TANK TRUCKS** Table of Contents




1. Rollover protection and protective housing for vapor/pressure supply valve at the top of the tank
2. Xmas tree with valve and gauge
3. Vacuum relief valve
4. Pressure relief valve
5. Manway
6. Clean out cap
7. Ground level vapor/pressure supply valve and fitting 1 ½" Camlock with ¾" Chicago (Crowsfoot) adapter
8. ¼" turn top vapor (vent) 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. Check that the temperature of the truck is less than 32°C (90°F) and above the freezing point of acrylic acid, 13°C (55°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 (77°F).
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.

## 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. Rail cars are typically equipped with coils which are 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 and facilitate the establishment of communications between the personnel at the emergency site and the supplier's emergency response team. 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 Rail Cars

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 35-45°C (95-113°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 electrical tracing temperature cannot exceed 35-45°C (95-113°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 ≤ 35-45°C is acceptable for this service because of their additional safety features. An independent high temperature shutdown at ≤ 35-45°C (95-113°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**. Frozen material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice. Such material may be either uninhibited or contain most of the inhibitor required for the entire contents of the tank car, depending on the method used to thaw the material. The acrylic acid 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 Rail Cars

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 storage 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 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.

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 and 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.

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.

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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, drain and disconnect the hose and fittings.
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 (IBC/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.

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.

Do to their increased size, mishandling of IBC (totes) of acrylic acid can have significantly worse consequences than with drums Extra care should be taken in the proper handling and transportation of IBC (totes) containing acrylic acid. Safe thawing and prevention of contamination can be difficult with IBC (totes), check with your supplier for specific recommendations.

### 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 Section 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 and facilitate the establishment of communications between the personnel at the site and the supplier's emergency response team. 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.
- Temperatures above 35-45°C (95-113°F) or 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.
- Conform to shelf life recommendations on your suppliers MSDS

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. Drums are not recycled. HDPE containers cannot be re-used in acrylic acid service if they contained other products because of the difficulty in effectively cleaning and removing potential contaminants from the HDPE.

### 9.6.3 Thawing Drums

**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. Frozen material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice.** Such material may be either uninhibited or it may contain most of the inhibitor required for the entire contents of the drum of the drum or IBC (TOTE), depending on the method used to thaw the material..

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 (e.g. 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 and polymerization of the low-inhibited monomer along the walls is easily initiated. Acrylic acid may be thawed by carefully applying limited heat (≤ 35-45°C) to the outside of a drum or IBC/tote.

### 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)*

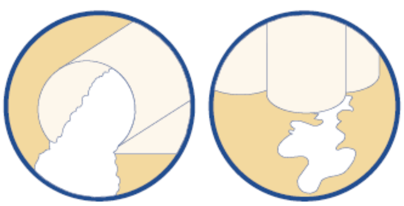
Acrylic acid is shipped in steel drums and IBC (totes) with polyethylene liners or self-supporting high density polyethylene drums and IBC (totes). When a carload or truckload of drums or IBC (totes) is received, leave the doors of the car or truck open for ventilation before entering. A persistent strong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



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# 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 some vaporization.

### 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. BAMM and its member companies believe the information below is factual; however, safe handling and compliance with federal, state and local laws and regulations is the responsibility of the company handling the acrylic acid.

A law called the Resource Conservation and Recovery Act (RCRA) and regulations promulgated thereunder must be followed if a volume of acrylic acid or material contaminated with acrylic acid is to be disposed of or discarded. Acrylic acid that is to be discarded or is off-specification, container residues, and spill residues are "listed hazardous wastes, code U008." 40 CFR 261.33. Materials mixed or contaminated with acrylic acid hazardous waste will likely also be hazardous waste upon disposal and will be subject to certain storage, handling and disposal restrictions as outlined in RCRA. 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. More details can be reviewed in 40 CFR 260-265 (the RCRA regulations). [See also http://www.epa.gov/epawaste/hazard/index.htm]

Many industries are subject to the Toxic Release Inventory requirements under EPCRA/SARA 313 and EPA's implementing regulations (40 CFR 372). (SARA Title III is the popular name for the Emergency Planning and Community Right-To-Know Act (EPCRA). SARA is the acronym for the Superfund Amendments and Reauthorization Act, which included EPCRA.) Acrylic acid is one of the chemicals for which releases to all environmental media must be annually reported by facilities subject to the regulations. [See http://www.epa.gov/tri/index.htm]

Acrylic acid is also subject to the Hazardous Substance inventory and hazard classification requirement of EPCRA/SARA 311 and 312 and its implementing regulations (40 CFR 355 and 370). Acrylic acid meets the following hazard categories for these programs: fire, reactive, acute health, and chronic health. [http://www.epa.gov/oem/content/epcra/epcra_storage.htm] Spills or releases of acrylic acid are subject to CERCLA (Superfund) Section 103 and EPCRA/SARA Section 304 reporting requirements for hazardous substances/hazardous chemicals.

Acrylic acid is regulated by the US EPA Risk Management Program (CAA 112(r) Risk Management Program), which requires a Process Hazard Analysis be completed by multifunctional teams EHS (Environmental, Health and Safety) reviews should be documented and subject to the management of change process developed for your facility.

### 10.2.2 Discharges to Navigable Waters

Discharges to streams and other navigable waters are controlled under federal and state regulations, including the National Pollutant Discharge Elimination System (NPDES) (40 CFR 122-125). The Clean Water Act is the primary US federal law governing discharges to surface waters. Both point-source (pipe and treatment point) and non-point-source (storm water) discharges may require permitting activities, including site-specific effluent limitations. Non-compliance with these limitations or discharge without an effluent permit is subject to significant civil and criminal penalties.

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### 10.2.3 Discharges to Municipal Sewers

Discharges to public sewers and treatment works are regulated by federal, state and local laws and 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, including the Clean Air Act and its implementing regulations. Acrylic acid is listed as a hazardous air pollutant (HAP) under Section 112 of the Clean Air Act; therefore facilities that emit acrylic acid may be subject to regulations directed at HAP. State regulations also control pollutants to the extent necessary to achieve or maintain national air quality standards as well as state-specific limitations. 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 RCRA regulations and state delegation of such regulation (see Section 10.2.1). 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 also 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 (see Section 10.2.1).

Any release of acrylic acid greater than the "reportable quantity" designated by the EPA under CERCLA (Superfund) Section 103 (See 40 CFR 302) or EPCRA/SARA Section 304 (see 40 CFR 355) should be reported immediately upon discovery, to the National Response Center (http://www.epa.gov/oswer/emergencies.htm and/or http://www.nrc.uscg.mil/nrchp.html) and State Emergency Response Agency (see current MSDS for reportable quantity and pertinent phone numbers). More details on reportable quantities can be reviewed in 40 CFR 302.4.

### 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. Check with the operator of the treatment works prior to doing so. 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 (see Section 10.2.1).

### 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 (See Section 11.2). Waste acrylic acid monomer may polymerize, creating additional hazards (see Section 6). Care should be taken to avoid mixing acrylic acid with incompatible materials or storing it in containers made of incompatible material, as noted in Sections 6.1, 6.5 and Appendix A (Incompatible Materials). 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, and 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. There may also be reporting requirements under CERCLA and EPCRA/SARA (see Section 10.3.1).

### 10.4. DISPOSAL OF WASTES

Acrylic acid is highly corrosive and should be handled with appropriate safety and personal protective equipment. Storage and disposal of acrylic acid waste is subject to RCRA regulation (see Section 10.2.1).

Acrylic acid may be sparingly 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. Do not introduce acrylic acid into a sewer without permission of the wastewater treatment plant owner.

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 Sections 6.1, 6.5 and Appendix A (Incompatible Materials).

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## 11 EMERGENCY RESPONSE

Signs of a potential emergency involving acrylic acid include increased temperatures (due to external heating or a polymerization exotherm), venting of the container, or container deformation. 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. A one page safety guide summary for emergency responders can be found in Appendix D.

## 11.1 DETECTION AND RESPONSE TO INCIPIENT POLYMERIZATION IN A STORAGE TANK

If a system is installed and operated with appropriate prevention measures 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 installation of a restabilization (shortstop) system for use in the event of incipient polymerization. This subsection includes discussion of the design and operation of such a restabilization system. 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.

### 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]. Besides heat, other possible causes of acrylic acid runaways are removal of the dissolved oxygen from the product and chemical contamination of the product either from introduced material or from use of a container made of incompatible material (see Section 6 and Appendix A). 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. Dry, oil-free 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, if present, 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 response to rising temperature, caused by the likely polymerization exotherm (see next section).

### 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. See discussion of temperature triggers Section 11.1.3.3.

### 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 Section 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. As a shortstop inhibitor, the addition of PTZ prevents the use of the acrylic acid as a monomer in a controlled polymerization reaction and therefore it is recommended that acrylic acid that has been shortstopped be disposed of and not used.

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. Also to reduce time needed for PTZ delivery, the PTZ should be dissolved in the solvent and stored in that form. The initial concentration of PTZ in the shortstop solution should not be higher than the solubility limit in the solvent at the minimum expected winter ambient temperature. Higher concentrations than the solubility limit could cause PTZ to crystallize out and plug the shortstop vessel outlet nozzle. Maintenance of the PTZ solution should be discussed with the supplier along with storage recommendations.

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 are satisfied:

- A temperature rise of greater than 5°C (9°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). AT 60°C (140°F) ALL PERSONNEL SHOULD BE EVACUATED TO ½ A MILE AWAY.**

##### *11.1.3.4 Mixing of Restabilization (Shortstop) Inhibitor*

The final concentration of PTZ in the acrylic acid to be shortstopped should be in the range of 200 to 1,000 ppm. Note, 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.

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. PTZ does not require that the acrylic acid have dissolved oxygen in order to be an effective inhibitor, therefore the gas can be inert (e.g., nitrogen).

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 are 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, unlike MEHQ, 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°C to -9°C (0°F to 16°F). 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 airflow rate is limited by an orifice located between the air cylinder and the pressure regulator.

Contact your supplier for further information on shortstop systems.

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**Figure 11-1: Acrylic Acid Shortstop System Example I** Table of Contents

This example illustrates some safety features discussed in this booklet, specifics of your own facility will determine details of your design. Not all equipment or instrumentation required for operability is shown. See Table 7-2 for key to symbols.

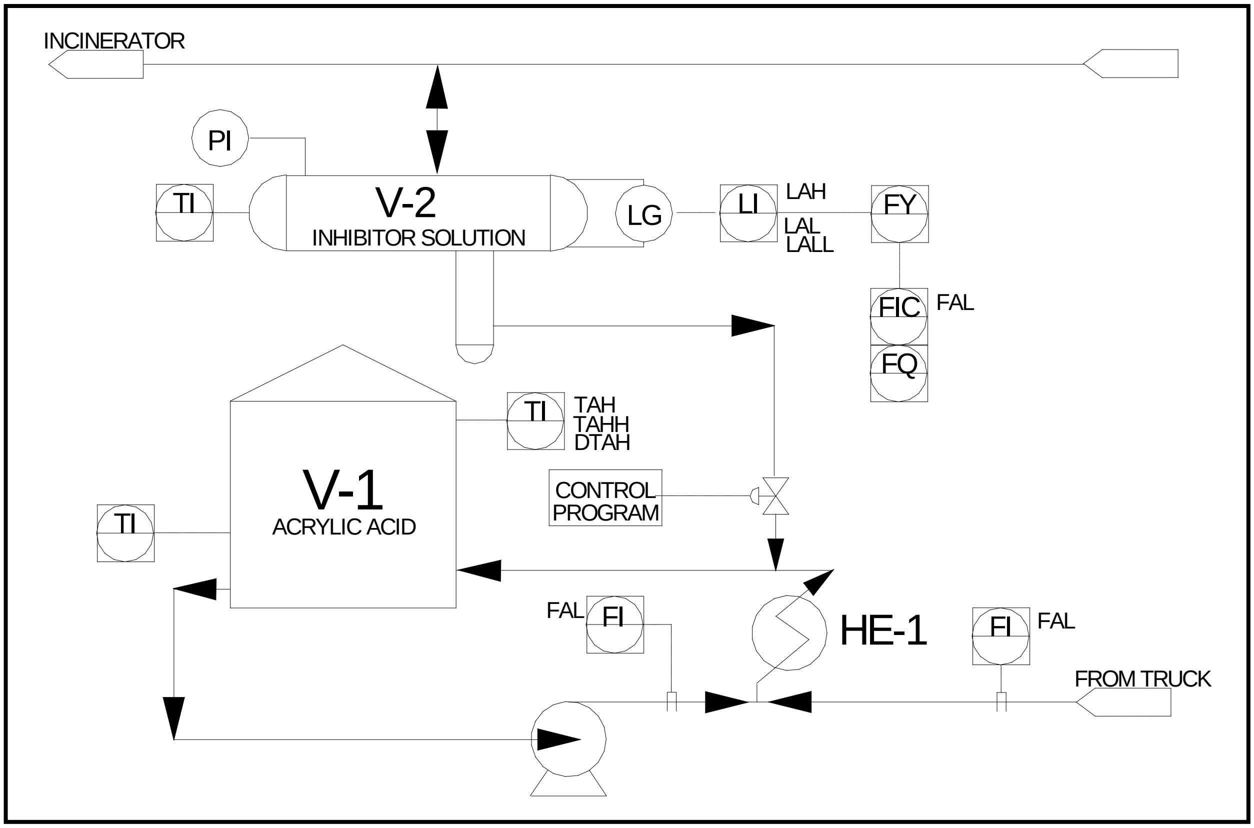
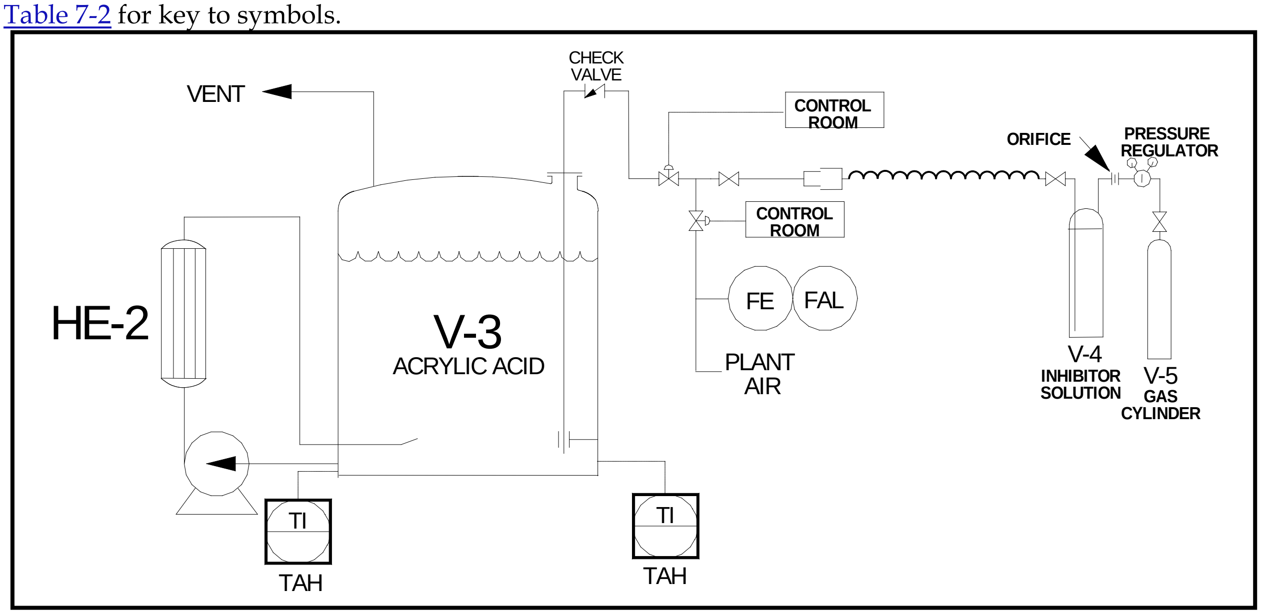



**Figure 11-2: Acrylic Acid Shortstop System Example II** Table of Contents

This example illustrates some of the safety features discussed in this booklet specifics of your own facility will determine details of your design. 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, Section 9.6)

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 of a ½ mile from the tank because of the risk of a runaway polymerization. At 60°C (140°F) all personnel should be evacuated to 1/2 mile.

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 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 shortstop agent should be added as quickly as possible and non-essential personnel should be evacuated. 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 (National Fire Prevention Association) 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.

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## APPENDIX A INCOMPATIBLE MATERIALS

Almost any contamination can potentially destabilize acrylic acid 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 promote rapid polymerization of the monomer.

1. chemicals with peroxide or peroxy- in the name
2. peresters or peroxyesters
3. percarbonates or peroxycarbonates
4. any other chemical with per in the name, e.g., t-butylperacetate
5. chemicals with hydroperoxide or hydroperoxy- in the 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. carboxylic acid anhydrides
17. mercaptans (thiols)
18. varnish
19. inert gases containing < 5% vol. % oxygen
20. carbon steel, brass and other metals susceptible to corrosion by acids
21. alloys containing copper, silver
22. metal salts

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## APPENDIX B Acrylic Acid Storage & Handling Safety Guide

Acrylic acid is a reactive chemical and must be handled carefully during storage and when loading. This guide summarizes acrylic acid handling "do's and don'ts". This guide should be used in conjunction with suppliers' MSDS and *Acrylic Acid: A Summary of Safety and Handling, 4th Ed. – 2013* (to which this is an appendix).

**NEVER OVERHEAT ACRYLIC ACID; KEEP BELOW 77°F (25°C)**

- Monitor acrylic acid storage temperature at all times. Maintain storage temperature above 59°F (15°C) to avoid freezing, and below 77°F (25°C) to maintain quality and stability.
- Never use steam to directly heat or thaw acrylic acid in a heat exchanger, tank or pipe.
- Never allow heat transfer fluid temperature to exceed 95-113°F (35-45°C)
- Never unload partially frozen containers of acrylic acid
- Use extreme caution if thawing frozen acrylic acid
- Never run pumps with outlet valves closed or blocked in.
- Never load acrylic acid into an empty container (i.e., trailer, railcar, drum, etc.) if it is hotter than 100°F (38°C).
- Never load "hot loads" over 90°F (32°C) next to an acrylic acid compartment, or load acrylic acid next to a "hot load".

**WARNING:**
If the temperature of the acrylic acid exceeds 90°F (32°C), or if an unexplained temperature increase of > 4°F (2°C) occurs, an emergency condition exists. Immediately contact supervision and CHEMTREC at 1-800-424-9300.

**EXTREME DANGER:**
If the temperature of acrylic acid reaches 140°F (60°C), an explosion is likely. Evacuate at least a ½ mile area surrounding the storage container/tank.

**NEVER USE PURE NITROGEN OR INERT GAS IN CONTACT WITH ACRYLIC ACID**

- Never use nitrogen or inert gas in contact with acrylic acid. Always use air or an air/nitrogen mixture that contains at least 5% oxygen in contact with acrylic acid. The inhibitor requires oxygen. Acrylic acid stabilized with a minimum concentration of 200 ppm PTZ does not require oxygen for the PTZ to be effective, nitrogen may be used after the addition of PTZ.

**NEVER ALLOW ACRYLIC ACID TO POLYMERIZE**

- Never contaminate stored acrylic acid with dirty hoses or load it into contaminated containers (vessels, trailers, railcars, totes, drums, etc.) It may violently polymerize (explode).
- Never allow acrylic acid to come in contact with carbon steel or brass
- Never store drums or totes in direct sunlight

**NEVER BE CARELESS**

- Contact supervision if acrylic acid is too hot (above 90°F /32°C), too cold (below 59°F /15°C) or if any of the external piping or systems are frozen.
- Spilled acrylic acid is very slippery. Clothing contaminated with acrylic acid will burn you. Properly dispose of contaminated clothing, leather gloves and footwear.
- Acrylic acid is corrosive and can cause severe burns of the skin and eyes (vision loss).
- Always wear goggles, face shield, acid gloves, and chemical protective clothing whenever contact with acrylic acid is possible (e.g., sampling, making & breaking connections).
- If you get acrylic acid on you, rinse with large amounts of water and get immediate medical attention.

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## APPENDIX C Acrylic Acid Transport Safety Guide

Acrylic acid is a reactive chemical and must be handled carefully during storage and transit. This guide summarizes acrylic acid handling "do's and don'ts". This guide should be used in conjunction with suppliers' MSDS and *Acrylic Acid: A Summary of Safety and Handling, 4th Ed. – 2013* (to which this is an appendix).

**NEVER OVERHEAT ACRYLIC ACID; ALWAYS KEEP BELOW 90°F**

- Record trailer temperature logs at every stop, or at least every 4 hours.
- Never use radiator water to heat acrylic acid.
- Use the in-transit heat exchanger to maintain acrylic acid above its freezing point (55 °F).
- Never use steam to warm or thaw acrylic acid.
- Never run pumps with outlet valves closed or blocked in.
- Never load trailers if they are hotter than 100°F (38°C).
- Never load 'hot loads' (over 90°F (32°C)) next to an acrylic acid compartment, or load acrylic acid next to a "hot load".

**WARNING:**
If the temperature of the acrylic acid exceeds 90°F (32°C), or if an unexplained temperature increase of > 4°F (2°C) occurs, an emergency condition exists. Park the trailer away from people and property and immediately contact supervision and CHEMTREC at 1-800-424-9300.

**EXTREME DANGER:**
If the temperature of acrylic acid reaches 140°F (60°C), an explosion is likely. Evacuate at least a ½ mile area surrounding the trailer.

**NEVER ALLOW ACRYLIC ACID TO POLYMERIZE**

- Never use nitrogen in contact with acrylic acid. Acrylic acid stabilized with a minimum concentration of 200 ppm PTZ does not require oxygen for the PTZ to be effective, nitrogen may be used after the addition of PTZ.
- Never contaminate acrylic acid with dirty hoses or load it into a contaminated trailer. It may violently polymerize (explode).

**NEVER BE CARELESS**

- Contact supervision and CHEMTREC at 1-800-424-9300 if a trailer containing acrylic acid is too hot (above 90°F).
- Contact supervision if a trailer containing acrylic acid is too cold (below 59°F) or if the outlet line is frozen.
- Spilled acrylic acid is very slippery.
- Clothing contaminated with acrylic acid will burn you. Properly dispose of contaminated clothing, leather gloves and footwear.
- Acrylic acid is corrosive and can cause severe burns of the eyes and skin and possibly cause permanent eye damage (loss of vision).
- Always wear goggles, face shield, acid gloves, and chemical protective clothing whenever contact with acrylic acid is possible (e.g., sampling, making & breaking connections).
- If you get acrylic acid on you, rinse with large amounts of water and get immediate medical attention.

## APPENDIX D Acrylic Acid Safety Guide for Emergency Responders

Acrylic acid is a very reactive chemical and must be handled carefully during any emergency. This guide summarizes the most important "do's and don'ts" regarding acrylic acid. This guide should be used in conjunction with suppliers' MSDS and *Acrylic Acid: A Summary of Safety and Handling, 4th Ed. – 2013 (*to which this is an appendix).

**Monitor acrylic acid temperature at all times.**
**The use of a remote temperature sensing device is recommended.**

**WARNING**

If the temperature of the acrylic acid exceeds **90°F (32°C)**, or if an unexplained temperature increase of > 4°F (2°C) occurs, an emergency condition exists.
All personnel should be moved out of the immediate area of the container or vessel. Contact CHEMTREC at 1-800-424-9300, if they have not already been contacted.

**EXTREME DANGER:**

If the temperature of acrylic acid reaches **140°F (60°C)**, an explosion is likely. Evacuate at least a ½ mile area surrounding the storage container/tank.

**Acrylic Acid will freeze at 55°F (13°C)**

Never use steam to directly heat or thaw acrylic acid in a heat exchanger, tank or pipe.
Never unload partially frozen containers of acrylic acid.
Never load acrylic acid into an empty container (i.e., trailer, railcar, drum, etc.) if the container is hotter than 100°F (38°C).

**NEVER USE PURE NITROGEN OR INERT GAS IN CONTACT WITH ACRYLIC ACID**

- Always use air or an air/oxygen mixture that contains at least 5% oxygen in contact with acrylic acid. The inhibitor will not work without oxygen. Acrylic acid stabilized with a minimum concentration of 200 ppm PTZ does not require oxygen for the PTZ to be effective, nitrogen may be used after the addition of PTZ.

**PREVENT RAPID ACRYLIC ACID SELF-POLYMERIZATION**

- Never contaminate stored acrylic acid with dirty hoses or load it into contaminated containers. (vessels, trailers, railcars, totes, drums, etc.)
- Never allow acrylic acid to come in contact with carbon steel or brass
- Never move acrylic acid from an emergency response site without adding PTZ stabilizer.

**PROTECTION OF EMERGENCY PERSONNEL**

- The minimum PPE is Level B as defined by 29CFR1910.120 appendix B.
- Spilled acrylic acid is very slippery.
- Acrylic acid is corrosive and can cause severe burns of the skin and eyes (vision loss) & Clothing & tools contaminated with acrylic acid will burn you.

Decontamination –

- Personnel – rinse 15 to 20 minutes with large amounts of water & remove contaminated clothing and get medical attention. Properly dispose of contaminated clothing, gloves and footwear.
- PPE/tools rinse with large amounts of water with or without detergent

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# APPENDIX E ACRYLIC ACID AUDIT AND ASSESSMENT PROTOCOL

The purpose of Appendix E is to provide an Audit and Assessment Protocol for acrylic acid inhibited with hydroquinone monomethyl ether (MEHQ, methoxyphenol), hereafter referred to as acrylic acid. (Commercial acrylic acid also is known as glacial acrylic acid, or GAA.) Acrylic acid is high purity acrylic acid stabilized with at least 180 parts per million by weight (ppm) of MEHQ. This acrylic acid audit and assessment protocol is an appendix to *Acrylic Acid: A Summary of Safety and Handling, 4th Edition – 2013,* published by the Basic Acrylic Monomer Manufacturers (BAMM) references to appropriate sections of that document are given at the start of each section below. For ease of reference, the document is abbreviated AAed4.

**ACRYLIC ACID AUDIT AND ASSESSMENT PROTOCOL CONTENTS**



## ACRYLIC ACID STORAGE

1. **Storage Tank Design Characteristics** ***(refer to AAed4 Section 7.2 Design consideration)***

Tanks used for acrylic acid storage should conform to certain minimum design characteristics to ensure safe storage.

**1.1. Tanks in acrylic acid service should be constructed of stainless steel.**

*Acrylic acid is corrosive to many other commonly used materials of construction. The products of corrosion can catalyze polymerization of* acrylic acid. *Other materials of construction might be* *acceptable, but need to be carefully reviewed to determine impact on acrylic acid stability. In no case should carbon steel or brass be used.*

**Records Review**

**1.1.1.** Are tanks in acrylic acid service constructed of stainless steel?

**1.1.2.** If not, has material of construction been evaluated for suitability?

**1.2. A floating roof tank is not recommended for acrylic acid storage.**

*A floating roof creates a seal or barrier between the* acrylic acid *and its source of oxygen replenishment above the roof. Use of a floating roof tank for acrylic acid storage dramatically increases the likelihood of a runaway polymerization.*

**Records Review**

**1.2.1.** Do tanks used to store acrylic acid have floating roofs?

**1.3. Dikes around storage tanks are used to contain spills.**

*Separation of flammables from acrylic acid prevents pool fire risk around acrylic acid tank.*

**Records Review**

**1.3.1.** Are dikes around storage tanks?

**1.3.2.** Is *acrylic acid* separate from other flammables?

**1.4. Water monitors, fixed water spray, or foam is suggested to help control acrylic acid fires and to cool acrylic acid containing equipment during a fire.**

**Records Review**

**1.4.1.** Are water monitors present? Coverage?

**1.4.2.** Fixed water spray present?

**1.5. Outdoor storage tanks should be insulated for freeze protection.**

**Records Review**

**1.5.1.** If outdoor storage tank, is it insulated?

**1.6. The storage tank should be equipped with vacuum and pressure relief valves unless the tank is open to the atmosphere. Relief of an unscheduled polymerization of acrylic acid requires a weak seam roof or its equivalent.**

**Records Review**

**1.6.1.** Is the tank equipped with vacuum and relief valves?

**1.6.2.** Is the tank equipped with a weak seam roof or its equivalent?

**1.7. Safety showers and eyewash fountains are recommended in the unloading and storage areas.**

**Records Review**

**1.7.1.** Are safety showers and eyewash fountains present?

## 2. Preventing Gross Contamination *(refer to AAed4 Section 6 Stability and Reactivity Hazards & Appendix A Incompatible materials )*

Gross contamination of *acrylic acid* with incompatible substances should be avoided. Some chemicals can cause a sudden runaway exothermic reaction that can result in violent venting or possibly an explosion of the vessel. It is not practical to design a shortstop system to handle gross contamination incidents involving neutralizing agents, oxidizers, or free-radical-producing chemicals (See AAed4 Appendix A). These classes of polymerization initiators result in a rapid, violent reaction that does not allow adequate time for the shortstop system to inhibit the polymerization.

**2.1. Contents should be positively identified as acrylic acid before it can be offloaded into the acrylic acid storage vessel. The preferred method of positive verification of the container contents is sampling the container at the receiving site for analysis.**

**Records Review**

**2.1.1.** What method of positive verification of container contents is practiced at the site?

**2.1.2.** Are there written procedures for this positive verification?

**2.2. Almost any contaminate can potentially destabilize acrylic acid and should be avoided. In most cases the compounds identified in AAed4 Section 6 and Appendix A as incompatible materials will cause polymerization of the monomer. This list of incompatibles should be readily available at the site and be part of the regular training.**

**Records Review**

**2.2.1.** Is the list of incompatible materials readily available?

**2.2.2.** Is the list of incompatible materials part of the regular training?

**2.2.3.** Was list of incompatible materials considered during design of facility and storage area?

## 3. Preventing Minor Contamination *(refer to AAed4 Section 6 Stability and Reactivity Hazards & Appendix A Incompatible materials )*

Contaminants can be introduced into the acrylic acid tank through in-plant activities such as dedicated tie-ins, temporary tie-ins, and cleaning/maintenance activities. Understanding what incompatibles are on the site is an important step in preventing contamination and an incipient runaway polymerization. With the activation of an effective shortstop system, the incipient polymerization may be stopped unless there is gross contamination.

**3.1. Incompatible materials (i.e., caustics, oxidizers, free radical producers such as peroxides, azides, aldehydes, ethers, and others listed in AAed4 Appendix A) should not be hard piped to an acrylic acid storage tank. Other tie-ins (vents, utilities, effluent, cleaning, instrument purges, heat transfer fluids, sparge gas, etc.) to the tank should be carefully reviewed to prevent contamination of the acrylic acid with incompatible substances.**

*Incompatible materials can cause an immediate, violent runaway polymerization.*

**Records Review**

**3.1.1.** Has a review been conducted to determine if there are contaminates hard piped (including inert gas) to an acrylic acid storage tank?

**3.1.2.** Has a review been conducted to determine if there is potential for contamination from other tie-ins to the tank to prevent contamination of the acrylic acid with incompatible substances?

**3.2. To decrease the likelihood of contamination, there should be a written procedure for both cleaning out an acrylic acid tank in preparation for modifications or inspection and returning an acrylic acid tank to service after internal tank inspection/maintenance is performed (AAed4 Section 8).**

**Records Review**

**3.2.1.** Is there a written procedure for returning an acrylic acid tank to service after internal tank inspection/maintenance is performed?

**3.2.2.** Is there a written procedure for the preparation and cleaning of an acrylic acid tank?

## *4.* Monitoring and Controlling Temperature *(refer to AAed4 Section 7.2.1 Temperature Control of Bulk Storage Tanks & Accessories )*

The temperature of acrylic acid should be controlled to ensure the stability of the material during storage. Since temperature rises may indicate the onset of a polymerization reaction, temperature monitoring is necessary to provide continuous indication of the stability of the acrylic acid. Detection of the temperature rise is necessary to prevent or inhibit the escalation of the incipient polymerization reaction to an uncontrolled violent reaction.

**4.1. Acrylic acid should be stored at a temperature between 15°C/59°F and 25°C/77°F.**

*Temperatures below 15°C/59°F are avoided to prevent freezing the* acrylic acid *(freezing point is 13°C/55°F) and avert the potential hazards associated with thawing. The formation of acrylic acid dimer accelerates at temperatures above 25°C/77°F (potential quality problem). Also, higher storage temperatures compromise the stability of* acrylic acid *and should be avoided.*

**Records Review**

**4.1.1.** Is acrylic acid stored between 15 °C (59°F) and 25 °C (77°F)?

**4.1.2.** If not, what is highest and lowest temperature for storage?

**4.2. Acrylic acid should not be stored longer than one year from its production date.**

*Even if all the storage conditions outlined in* AAed4 *associated with temperature, inhibitor, dissolved oxygen, and contamination are met;* acrylic acid *should not be stored for longer than one year due to peroxide build-up. Deviation from these conditions may significantly shorten the safe storage life.*

**Records Review**

**4.2.1.** Is there a system in place that assures that acrylic acid is not stored longer than one year?

**4.3. Never use the direct application of live steam, steam tracing, or steam coils to heat or thaw acrylic acid.**

*There is no practical way to limit and control the temperature of steam below the maximum allowed storage temperature of 35-45°C (95-113°F) for* acrylic acid.

**Records Review**

**4.3.1.** Is steam used to heat or thaw acrylic acid?
**4.3.2.** What is temperature maximum of heating medium?

**4.4. The acrylic acid tank should be equipped with two or more temperature sensors that are continuously monitored by personnel at a remote control facility.**

- **Each of the temperature sensors should be independent and reliable.**
- **The temperature sensors should be installed at a sufficient distance from the liquid recirculation inlets (including eductors) so that the indicated temperature is truly representative of the bulk liquid temperature, and not of the recirculation material entering the tank.**
- **Two sensors should be located with at least 90 degrees radial separation to measure temperatures in different regions of the tank.**
- **The temperature sensors should be installed at a level that will always be submerged by acrylic acid. A minimum level of liquid should be maintained according to site-specific standard operating procedures (SOP).**

*Reliable temperature monitoring is critical for safe storage and detection of incipient polymerization events*

**Records Review**

**4.4.1.** Are the acrylic acid tanks equipped with two or more temperature sensors that can be continuously monitored by personnel at a remote control facility?
**4.4.2.** Do drawings reflect two temperature sensors that have 90 degrees radial separation and are installed at a sufficient distance from the liquid recirculation inlets so that the indicated temperature is truly representative of the bulk liquid temperature?
**4.4.3.** Are the temperatures independent and reliable?
**4.4.4.** Are the temperature indicators submerged at all times there is liquid in the tank?
**4.4.5.** Is there an SOP that defines the minimum level of liquid in the tank?

**4.5. Alarms should be installed to alert personnel if any temperature sensor detects an abnormally high or low temperature.**

- **A low temperature alarm should be set no lower than 15°C/59°F.**
- **A high temperature alarm should be set no higher than 25°C/77°F.**
- **Temperatures equal to or greater than 32°C/90°F should be investigated immediately**
- **A Hi-Hi alarm should be set no higher than 45°C/113°F.**
- **There should be a written procedure that describes the response to temperature alarms, and personnel should be trained on that procedure. This procedure should require activation of the shortstop system.**

- **A "Rate of Temperature Rise" detection system is recommended if equipment allows (see shortstop section).**

*The low temperature alarm indicates the potential for freezing acrylic acid. The high temperature alarm indicates that* acrylic acid *temperatures exceed the normal operating range and may indicate a polymerization reaction. The Hi-Hi temperature alarm (45°C/113°F) warns of an incipient polymerization event and is an activation criterion for the shortstop system).*

### Records Review

**4.5.1.** Do the acrylic acid tanks contain alarms that are set:
- Low temperature, no lower than 15°C/59°F?
- High temperature, no higher than 25°C/77°F?
- HI-Hi temperature, no higher than 45°C/113°F?

**4.5.2.** Is the shortstop system activated no higher than 45°C/113°F?
**4.5.3.** Is there a written procedure that describes the response to temperature alarms?
**4.5.4.** Are personnel trained on the procedure for response to temperature alarms?
**4.5.5.** Are temperatures above 32°C/90°F investigated immediately?

**4.6. Tank contents should be continuously circulated through a properly designed eductor to ensure good mixing.**

- **Circulation should be maintained.**
- **Any fault that interrupts this circulation (e.g., deadheaded pump trip) should be corrected promptly.**
- **The circulation return line should contain an eductor(s).**

*A properly-designed eductor(s) ensures uniform inhibitor levels, representative temperature measurements, and uniform dissolved oxygen distribution.*

### Records Review

**4.6.1.** Is the circulation maintained on the tank?
**4.6.2.** Does the circulation return line contain an eductor?

**4.7. Thawing frozen acrylic acid and acrylic acid tank temperature control should be accomplished under controlled conditions:**

- **Never use live steam or steam tracing on the outside of a vessel, line, or any other piece of equipment containing acrylic acid.**
- **The preferred tank temperature control and thawing method for acrylic acid is a tempered water system where the heating and cooling of the tempered water is accomplished by indirect heat exchange, e.g. a shell and tube heat exchanger. Protection should be included to ensure that the tempered water temperature is maintained below 35-45°C/95-113°F.**
- **If electrical heat tracing is used to prevent acrylic acid from freezing or to thaw frozen acrylic acid in pumps, valves, piping, and vessels, the heat tracing should:**
    - **Be installed per the manufacturer's instruction,**

- **Meet all electrical codes and standards applicable for the location where the tracing is installed, and**
- **Have an independent temperature-limiting device set no higher than 35-45 °C/95-113° F and this device should be functionally checked. Depending on installation, multiple temperature limiting devices may be required to properly protect the acrylic acid.**

- **Never remove material from a partially-thawed vessel. After thawing, the dissolved oxygen and inhibitor should be redistributed. In storage tanks, the existing recirculation system should adequately redistribute dissolved oxygen and inhibitor.**

*When frozen acrylic acid is thawed, the resulting liquid is depleted in dissolved oxygen, which should be replenished.*

*When acrylic acid partially freezes, the remaining liquid contains most of the MEHQ, leaving the solid portion inhibitor deficient. If the remaining liquid is removed, then the thawed solid portion is extremely dangerous because of its lack of MEHQ. Frozen material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice.*

### Records Review

If the site uses tempered water to control the temperature of acrylic acid or thaw acrylic acid,

**4.7.1.** Is the tempered water controlled between 15 °C (59°F) and 35-45 °C (95-113°F)?

**4.7.2.** Is the heating and cooling of the tempered water accomplished by indirect heat exchange?

**4.7.3.** Does the tempered water system include protection to ensure the tempered water does not exceed 35-45 °C (95-113°F)?

If the site uses electrical heat tracing to thaw acrylic acid,

**4.7.4.** Is the tracing installed per the manufacturer's instructions?

**4.7.5.** Does tracing meet all codes and standards applicable for the location where the tracing is installed?

**4.7.6.** Does the tracing have redundant temperature-limiting devices set no higher than 35-45°C (95-113°F)?

**4.7.7.** Are the temperature-limiting devices functionally checked?

## *5.* Controlling Dissolved Oxygen *(refer to AAed4 Section 6 Instability and Reactivity Hazards & Section 7 Bulk Storage Facilities and Accessories)*

Glacial acrylic acid is inhibited with monomethyl ether of hydroquinone (MEHQ). MEHQ stabilizes acrylic acid with respect to polymerization ONLY if dissolved oxygen is present.

**5.1. Acrylic acid should be stored under a blanket atmosphere containing 5 to 21 volume % oxygen in order to maintain the required dissolved oxygen for inhibition. This can be achieved by a blended gas system with the proper controls or by air. Dry, oil free air is preferred.**

### Records Review

**5.1.1.** Is there a system in place to assure that acrylic acid is stored under a blanket atmosphere that contains 5 to 21 volume % oxygen?

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**5.2. Any gas blending system used to generate a reduced-oxygen atmosphere for acrylic acid service should have protection with high and low oxygen concentration alarms to ensure a controlled gas composition. The layers of protection may be either oxygen analyzers or a ratio of flow meters.**

### Records Review

**5.2.1.** Does the blend gas system have two independent layers of protection for oxygen content and a documented maintenance program?

**5.3. Acrylic acid in storage should be circulated through a properly designed eductor(s) to replenish the dissolved oxygen by contact with the blanket gas.**

### Records Review

**5.3.1.** Does the tank have an eductor?
**5.3.2.** Is there a system in place to ensure interruptions in circulation are corrected promptly?

**5.4. A minimum of 10% outage should be maintained in acrylic acid tanks.**

*This ensures an adequate volume of an oxygen-containing blanket above the liquid to maintain the dissolved oxygen concentration in the acrylic acid.*

### Records Review

**5.4.1.** Is a minimum of 10% outage maintained in acrylic acid tanks?
**5.4.2.** Is there a high level alarm at 90%?

**5.5. An inert gas (one containing less than 5 volume % oxygen) should never be used in acrylic acid service. Specific examples include:**

- **Inert gas should not be used as blanket gas or as barrier gas for dual seal pumps.**
- **Inert gas should not be used as motive gas for making transfers, blowing lines, pigging lines, etc.**
- **Inert gas should not be used for sparging an acrylic acid tank, or for purging a vessel or instrument line to be used in acrylic acid service.**
- **Inert gas should not be hard-piped to an acrylic acid tank.**

*Any inert gas in contact with acrylic acid can potentially defeat the MEHQ-oxygen inhibitor system.*

*Nitrogen or inert gas is acceptable to blow PTZ shortstop solution into an acrylic acid tank. After shortstop injection, the shortstopped acrylic acid becomes PTZ-inhibited acrylic acid and does not require oxygen for inhibitor effectiveness.*

### Records Review

**5.5.1.** Is inert gas used as a blanket gas or as a motive gas for making transfers, blowing lines, pigging lines, barrier gas on dual seal pumps, etc.?
**5.5.2.** Is inert gas used for sparging acrylic acid or for purging a vessel or instrument line to be used in acrylic acid service?
**5.5.3.** Is inert gas hard piped to an acrylic acid tank?

**5.6. In case of inadvertent purging of acrylic acid with an inert gas, the acrylic acid should be sparged with air as or blended gas with 5-21% oxygen soon as possible.**

*Purging of acrylic acid with an inert gas may result in acrylic acid that has no dissolved oxygen, a situation that defeats the MEHQ inhibitor.*

### Records Review

**5.6.1.** Is there a procedure in place so that, in the case of inadvertent purging of acrylic acid with an inert gas, the acrylic acid is sparged with air as soon as possible?

**5.7. The dissolved oxygen and inhibitor should be redistributed after thawing. In storage tanks, the existing recirculation system should adequately redistribute dissolved oxygen and inhibitor.**

*When frozen acrylic acid is thawed, the resulting liquid is depleted in dissolved oxygen, which should be replenished.*

*When acrylic acid partially freezes, the remaining liquid contains most of the MEHQ, leaving the solid portion inhibitor deficient. If the remaining liquid is removed, then the thawed solid portion is extremely dangerous because of its lack of MEHQ. Frozen material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice.*

### Records Review

**5.7.1.** Is there a system to ensure that if the contents of a thawed rail car or truck are not transferred to a storage tank within 24 hours, the vessel is appropriately agitated and /or aerated?

## *6.* Ensuring Inhibition *(refer to AAed4 Section 6 Stability and Reactivity Hazards)*

Glacial acrylic acid is inhibited with monomethyl ether of hydroquinone (MEHQ) at a minimum concentration of 180 ppm. A*crylic acid* stored under conditions described in this minimum standard has a stability time of one year. MEHQ stabilizes *acrylic acid* only if dissolved oxygen is present.

**6.1. Acrylic acid should contain a minimum of 180 ppm of MEHQ inhibitor.**

*Even if all the conditions of this standard associated with temperature, inhibitor, dissolved oxygen, and contamination are met, acrylic acid should not be stored for longer than one year due to peroxide build-up. Failure to meet the conditions of this standard may significantly shorten the safe storage life.*

### Records Review

**6.1.1.** Is there a system to ensure that acrylic acid contains 180 ppm of MEHQ inhibitor?
**6.1.2.** Is there a system to ensure that acrylic acid is not stored for longer than one year?

## *7.* Shortstopping Incipient Runaway Polymerizations *(refer to AAed4 Section 11.1 Detection and Response to Incipient Polymerization in a Storage Tank)*

Once a polymerization has begun (by a method other than gross contamination), there is a time interval in which the reaction can be shortstopped. The shortstop system contains a powerful inhibitor, phenothiazine (PTZ) that is effective at high temperatures and in the absence of oxygen

**7.1. It is recommended that all acrylic acid storage tanks have access to a system for shortstopping incipient runaway polymerizations. 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.**

### Records Review

**7.1.1.** Do all acrylic acid storage tanks have access to a system for shortstopping incipient runaway polymerizations?

**7.2. The initial concentration of PTZ in the shortstop solution should not be higher than the solubility limit in the solvent at the minimum expected winter ambient temperature. Charges of the shortstop solution should be analyzed on receipt to verify the design concentration and checked periodically.**

*Higher concentrations than the solubility limit could cause PTZ to crystallize out and plug the shortstop vessel outlet nozzle.*

### Records Review

**7.2.1.** Is the initial concentration of PTZ in the shortstop inhibitor solution greater than the solubility limit in the solvent at the minimum expected winter ambient temperature?
**7.2.2.** Is the shortstop solution analyzed on receipt to verify design concentration?
**7.2.3.** Is the PTZ concentration checked periodically?

**7.3. The shortstop system should be designed to deliver PTZ solution to achieve a final mix-out concentration of PTZ in the acrylic acid tank in the range of 200 to 1000 ppm.**

### Records Review

**7.3.1.** Has a mixing analysis been done to ensure the system as designed will result in a final mix-out concentration of PTZ in the acrylic acid of at least 200 PPM?

**7.4. Product temperatures of 32°C/90°F or higher can be hazardous and should be immediately investigated.**

*Investigation must include determining the cause for the abnormally high temperature and correcting that cause. Failure to correct could jeopardize the stability of the acrylic acid and necessitate emergency response*

### Records Review

**7.4.1.** Are procedures in place to initiate an investigation if the temperature of stored acrylic acid reaches 32°C/90°F or higher?

7.5. **Shortstop activation criteria:**

- **For acrylic acid vessels with two remote temperature sensors installed, the shortstop system should be activated when either of the temperature sensors reaches 45°C/113°F.**
- **For acrylic acid vessels with three remote temperature sensors installed, the shortstop system should be activated when two of the three temperature sensors reach 45°C/113°F.**
- **The shortstop system should be activated whenever the acrylic acid has been contaminated with a known or potential polymerization initiator.**
- **If the acrylic acid temperature rise exceeds 5°C/9°F in a 60 minute period or less, for no known reason, the shortstop system should be activated.**
- **There is a fire near the acrylic acid tank.**

*In the event of a severe fire near or with acrylic acid, when the acrylic acid liquid temperature reaches 50°C/122°F it is necessary to evacuate all non-essential personnel to a distance of 1/2 mile from the tank because of the risk of a runaway polymerization. At 60°C/140°F* ***ALL*** *personnel should be evacuated to ½ mile.*

**Records Review**

**7.5.1.** For acrylic acid vessels with two remote temperature sensors installed, is the shortstop system activated when either of the temperature sensors reaches 45°C?
**7.5.2.** For acrylic acid vessels with three remote temperature sensors installed, is the shortstop system activated when two of the three temperature sensors reach 45°C?
**7.5.3.** Is the shortstop system activated whenever the acrylic acid has been contaminated with a known or potential polymerization initiator?
**7.5.4.** Is the shortstop system activated whenever there is a temperature rise exceeding 5°C/9°F in a 60 minute period or less, for no known reason?
**7.5.5.** Is the shortstop system activated whenever there is a fire near the acrylic acid tank?
**7.5.6.** Are all non-essential personnel evacuated at 50°C/122°F?
**7.5.7.** Are all personnel evacuated at 60°C/140°F?

7.6. **There should be a written procedure for activation of the shortstop system, and personnel should be trained periodically on that procedure.**

**Records Review**

**7.6.1.** Is there a written procedure for activation of the shortstop system?
**7.6.2.** Are people trained periodically on the written procedure for activation of the shortstop system?
**7.6.3.** Is the system kept evergreen by periodic testing and dry runs (equipment, procedures, and shortstop analysis)?

*8.* **Pumps, Piping, Miscellaneous** ***(refer to AAed4 Section 7.0 Bulk Storage Facilities and Accessories)***

Proper design of ancillary systems on an acrylic acid tank contributes to the safe storage and handling of acrylic acid. The pumps used to circulate and transfer acrylic acid should conform to minimum design standards. Piping systems used in conjunction with acrylic acid storage tanks should be designed to minimize the possibility of inadvertent polymerization and oxygen-stripping. Use proper materials of construction for pump seals, gaskets, hoses (AAed4 Section 7.2.8))

**8.1. All pumps and piping in acrylic acid service should be dedicated to acrylic acid service and constructed from stainless steel.**

*Acrylic acid is corrosive to other commonly-used materials of construction. The products of corrosion can catalyze polymerization of acrylic acid.*

*Other materials of construction might be acceptable, but need to be carefully reviewed to determine impact on acrylic acid stability. Do not use carbon steel or brass.*

**Records Review**

**8.1.1.** Are all pumps and piping in acrylic acid service dedicated to acrylic acid service and constructed from stainless steel?

**8.2. Acrylic acid pumps should be instrumented to protect against "deadhead" (or blocked-in) situations. Pump deadhead protection should be present.**

**Records Review**

**8.2.1.** Are acrylic acid pumps instrumented to protect against "deadhead" situations?

**8.3. Incompatible materials (i.e., caustics, oxidizers, free radical producers such as peroxides, azides, aldehydes, ethers, and others listed in AAed4 Appendix A) should not be connected to a dedicated acrylic acid line. Other tie-ins (vents, utilities, effluent, cleaning, instrument purges, heat transfer fluids, sparge gas, etc.) to dedicated acrylic acid lines should be carefully reviewed to prevent contamination of the acrylic acid with incompatible substances.**

*Incompatible materials can cause an immediate, violent runaway polymerization.*

**Records Review**

**8.3.1.** Has a review been conducted to determine if there are contaminates hard piped to a dedicated acrylic acid line?

**8.3.2.** Has a review been conducted to determine if there is potential for contamination from other tie-ins to the acrylic acid lines to prevent contamination of the acrylic acid with incompatible substances?

**8.4. Steam tracing should never be used on acrylic acid circulation and transfer lines or pumps.**

*Steam tracing is not an acceptable choice for freeze protection. There is no way to control the temperature of the steam to be below 35-45°C/95-113°F - the maximum allowable temperature for thawing frozen acrylic acid).*

**Records Review**

**8.4.1.** Is steam tracing used on *acrylic acid* circulation lines, transfer lines, or pumps?

**8.5. Self-limiting or constant wattage electrical heat tracing limited to temperatures below 65°C and instrumented to control at less than or equal to 35-45°C may be used in *acrylic acid* service. An independent high temperature shutdown at less than or equal to 35-45°C may also be included as an additional safety feature.**

**Records Review**

If the site uses electrical heat tracing to thaw *acrylic acid*,

**8.5.1.** (a) Does the tracing have an intrinsic self-limiting temperature no higher than 65°C/149°F?

**8.5.2.** (b) Does the tracing have an independent control system limiting its temperature to 35-45°C/95-113°F?

**8.6. For thawing acrylic acid lines, see the appropriate portions of Section 7.1 of AAed4.**

**Records Review**

If the site uses tempered water to thaw frozen *acrylic acid* lines,

**8.6.1.** Is the tempered water controlled between 15°C/59°F and 35- 45°C/95-113°F?

**8.6.2.** Is the heating and cooling of the tempered water accomplished by indirect heat exchange?

**8.6.3.** Does the tempered water system include protection to ensure the tempered water does not exceed 35-45°C/95-113°F?

**8.7. Tempered water for tracing on acrylic acid circulation and transfer lines or pumps should conform to Section 7.2.1 of AAed4**

**Records Review**

If the site uses tempered water to trace acrylic acid lines or pumps,

**8.7.1.** Is the tempered water controlled between 15°C/59°F and 35-45°C/95-113°F?

**8.7.2.** Is the heating of the tempered water accomplished by indirect heat exchange?

**8.7.3.** Does the tempered water system include protection to ensure the tempered water does not exceed 35-45°C/95-113°F?

**8.8. Acrylic acid should never come into contact with any gas containing less than 5% oxygen. See Section 7.1 of AAed4**

**Records Review**

**8.8.1.** Does acrylic acid contact any gas containing less than 5% oxygen?

## DISTRIBUTION OF ACRYLIC ACID

Acrylic acid is transported in rail tank cars (T/C), tank trucks (T/T). Other shipping containers may be acceptable, but need to be evaluated for safe shipping.

### *9.* Shipping Container Design Characteristics (*refer to AAed4 Section 9*)

Shipping containers used for acrylic acid transportation should conform to certain minimum design characteristics to ensure safety.

**9.1. Bulk shipping containers (T/C and T/T) in acrylic acid transportation service should be constructed of stainless steel or aluminum. Drums used for acrylic acid transportation should be constructed of high-density polyethylene (HDPE). Totes should be constructed of HDPE, stainless steel or aluminum. Proper gaskets must be used (Section 7.2.8)**

*Acrylic acid is corrosive to many other commonly used materials of construction. The products of corrosion can catalyze polymerization of acrylic acid. Other materials of construction might be acceptable, but need to be carefully reviewed to determine impact on acrylic acid stability. Do not use carbon steel or brass.*

**Records Review**
What are the materials of construction for the shipping containers? If not HDPE, stainless steel or aluminum, have the materials been reviewed for impact on acrylic acid stability?

**9.1.1.** T/C
**9.1.2.** T/T
**9.1.3.** Totes
**9.1.4.** Drums

**9.2. T/Cs used for acrylic acid transportation should be insulated to protect against temperature extremes.**

*Low temperatures are a concern due to freezing and thawing problems. High temperatures can lead to accelerated dimer formation and shortened shelf life. Only indirect heating is allowed.*

**Records Review**
**9.2.1.** Are the T/C insulated?

**9.3. Trucks that are heated during transit should have a temperature indicator.**

**Records Review**
**9.3.1.** Do trucks that are heated during transit have temperature indicators for cargo?
**9.3.2.** Do trucks that are heated during transit have temperature indicators for heating medium?

## *10.* Preventing Gross Contamination *(reference AAed4 Section 6 Stability and Reactivity Hazards & Appendix A ( Incompatible materials) & Section 9 )*

Gross contamination of acrylic acid with incompatible substances should be avoided. Some chemicals can cause a sudden runaway exothermic reaction that can result in violent venting or possibly an explosion of the vessel.

**10.1. Before a shipping container can be loaded with acrylic acid it should be ensured that the container is clean or that the last contents were acrylic acid.**

*A common practice is to load acrylic acid into a container that last contained acrylic acid without cleaning that container. However, if a container had a previous cargo other than acrylic acid, that container should be cleaned prior to loading with acrylic acid.*

**Records Review**

**10.1.1.** Is there protection to insure that the container is clean or that the last contents were acrylic acid?

**10.1.2.** If dedicated, have procedures at receiving end been checked to ensure that contamination is avoided?

**10.2. Protection is required to verify that a container carries acrylic acid before it can be transloaded into a different acrylic acid container. One of these should be a positive verification of the container contents (e.g. analysis, specific gravity) by sampling the container at the receiving site. These protections should be documented in written procedures.**

**Records Review**

**10.2.1.** Is protection employed before acrylic acid is transloaded?

**10.2.2.** Is positive identification of contents required?

**10.2.3.** Is there a written SOP?

## *11.* Preventing Minor Contamination (*refer to AAed4 Section 6 Stability and Reactivity Hazards & Appendix A Incompatible materials* )

Acrylic acid shipments can become contaminated from:

- heels of previous cargoes
- inadequate cleaning
- contaminated hoses and pumps
- vent line over-pressuring
- errors during the loading process
- other possible causes.

If the contamination involves a substance that is incompatible with acrylic acid, then a polymerization reaction may ensue that can result in violent venting or possibly an explosion of the vessel.

**11.1. Drums used for shipping acrylic acid should be new. Metal totes used for shipping acrylic acid should be new, dedicated or cleaned. Totes made of HDPE should be new or dedicated to acrylic acid service.**

*Drums are not recycled. HDPE totes cannot be re-used in acrylic acid service if they contained other products because of the difficulty in effectively cleaning and removing potential contaminants from the HDPE.*

**Records Review**

**11.1.1.** Are new drums used for shipping acrylic acid?

**11.1.2.** Are metal totes new, dedicated or cleaned?

**11.1.3.** If totes are made of HDPE, are they new?

**11.2. Incompatible materials (i.e., caustics, oxidizers, free radical producers such as peroxides, azides, aldehydes, ethers, and others listed in *Acrylic Acid A Summary of Safety and Handling* Appendix A should not be allowed to come into contact with acrylic acid during the loading process or in the transport container.**

**Tie-ins to the loading system lines (vents, vent scrubbers, utilities, effluent, cleaning, instrument purges, heat transfer fluids, sparge gas, etc.) should be carefully reviewed to prevent contamination of the acrylic acid with incompatible substances.**

*Incompatible materials can cause an immediate, violent runaway polymerization.*

**Records Review**

**11.2.1.** Have tie-ins to the loading system been reviewed to prevent contamination with incompatibles?

**11.3. There should be written cleaning procedures for T/Ts, T/Cs, and totes, to prevent returning a container to service that still contains residual cleaning chemicals.**

*Caustics or other incompatible materials may be left as a residue after cleaning is performed on containers.*

**Records Review**

**11.3.1.** Are there written procedures for cleaning T/Ts, T/Cs, and totes?

**11.4. Acrylic acid should not remain in a shipping container beyond one year from its production date.**

**If acrylic acid has been in a shipping container beyond one year, it should be stabilized by the addition of at least 200 ppm PTZ and disposed of at a licensed facility**

*Even if all the storage conditions described in AAed4 associated with temperature, inhibitor, dissolved oxygen, and contamination are met; acrylic acid should not remain in the shipping container for longer than one year due to peroxide build-up. Failure to meet all of the recommended storage conditions may significantly shorten the safe storage life.*

**Records Review**

**11.4.1.** Is acrylic acid stored in a shipping container for longer than one year?

**11.4.2.** If stored for longer than one year, is at least 200 ppm PTZ added?

## *12.* Monitoring and Controlling Temperature *(refer to AAed4 Section 9 Safe Transport of Acrylic Acid, & Section 7.2.1 Bulk Storage Facilities and Accessories)*

Temperatures below 15°C/59°F are avoided to prevent freezing the acrylic acid (freezing point is 13°C/55°F) and avert the potential hazards associated with thawing. The formation of acrylic acid dimer accelerates at temperatures above 25°C/77°F (potential quality problem). Also, higher storage temperatures compromise the stability of acrylic acid and should be avoided.

In T/Ts, acrylic acid cargoes are heated during seasonally cold temperatures to prevent freezing on long hauls. T/T product temperatures are monitored at regular intervals. T/C temperatures are not controlled or monitored in transit. Drums and totes are usually transported in heated trucks to prevent freezing.

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**12.1. Never use the direct application of live steam in tracing or coils to heat or thaw acrylic acid.**

*There is no practical way to limit and control the temperature of steam below the maximum allowed temperature of 35-45°C/95-113°F for the heating medium.*

**Records Review**

**12.1.1.** Is live steam used to thaw acrylic acid?

**12.2. When heating during transit (e.g., T/T during winter), the acrylic acid container should be equipped with a temperature sensor that is monitored every four hours.**

**Direct heating of acrylic acid with tractor radiator water is not acceptable due to its high temperature.**

**If the temperature of the acrylic acid container is discovered to be greater than 32°C/90°F at any time during the distribution process, the contents of that shipping container are suspected to be undergoing an inadvertent polymerization. Hence, the responsible party (e.g., carrier or customer) should immediately notify CHEMTREC (1-800-424-9300). CHEMTREC will notify the supplier and facilitate the establishment of communications between the personnel at the site and the supplier's emergency response team.**

**Records Review**

**12.2.1.** When heated during transit or transported in high ambient temperatures without cooling, is the T/T temperature monitored every four hours?

**12.2.2.** If the temperature exceeds 32°C/90°F, is CHEMTREC notified?

**12.3. If drums or totes are to be prevented from freezing during transportation, then the temperature of the storage compartment containing the drums and totes should be maintained between 15°C/59°F and 25°C/77°F.**

**Records Review**

**12.3.1.** During winter shipment, is the storage compartment maintained between 15°C/59°F and 25°C/77°F for drums and totes?

**12.4. A safe thawing procedure should be followed if acrylic acid is allowed to freeze during transportation.**

*When acrylic acid partially freezes, the remaining liquid contains most of the MEHQ, leaving the solid portion inhibitor deficient. If the remaining liquid is removed, then the thawed solid portion is extremely dangerous because of its lack of MEHQ. Thawing sometimes involves applying heat to the under-inhibited solid portion, making compliance with the upper temperature limits (see below) even more critical.*

**Thawing frozen acrylic acid should be accomplished under controlled conditions:**

- **Never use live steam or steam tracing on the outside of a vessel, line, or any other piece of equipment containing acrylic acid.**
- **The preferred thawing method for bulk acrylic acid containers is a tempered water system where the heating and cooling of the water is accomplished by indirect heat exchange, e.g. a shell and tube heat exchanger. Protection should be included to ensure that the water temperature is maintained below 35-45°C/95-113°F.**
- **If electrical tracing is used to prevent acrylic acid from freezing or to thaw frozen acrylic acid in pumps, valves, piping and vessels, the heat tracing should:**
  - **be installed per the manufacturer's instructions,**
  - **meet all electrical codes and standards applicable for the location where the tracing is installed, and**
  - **Have an independent temperature-limiting device set no higher than 35-45°C/95-113°F, and this device should be functionally checked.**
- **Frozen acrylic acid in T/Cs should be thawed by circulating tempered water through the container's coils. The temperature of the tempered water should be less than or equal to 35-45°C/95-113°F.**
- **Acrylic acid drums and totes should be thawed by placing the containers in a heated room at a temperature between 20°C/ 68°F and 33°C/91°F. Generally, about 48 hours results in a thawed drum. Containers should be agitated periodically to mix inhibitor and dissolved oxygen during thawing (e.g. drum roller, tote agitator, pallet shaker)**
- **Never remove material from a partially-thawed vessel. After thawing, the dissolved oxygen and inhibitor should be redistributed. Inhibitor and oxygen should be redistributed in drums by rolling the drums, or by injecting air. Frozen material remaining in a vessel after unloading may create a potentially dangerous condition, in the event frozen material remains after unloading, contact your supplier for advice.**

*When frozen acrylic acid is thawed, the resulting liquid is depleted in dissolved oxygen, which should be replenished. When acrylic acid partially freezes, the remaining liquid contains most of the MEHQ, leaving the solid portion inhibitor deficient. If the remaining liquid is removed, then the thawed solid portion is extremely dangerous because of its lack of MEHQ.*

**Records Review**

**12.4.1.** Is steam used to thaw frozen acrylic acid?
**12.4.2.** If a tempered water system is used, is there protection to ensure that the water is maintained below 35-45°C/95-113°F?
**12.4.3.** If electrical tracing, are there temperature limiting devices set no higher than 35-45°C/95-113°F?
**12.4.4.** For T/Cs is tempered water used with the water temperature maintained below 35-45°C/95-113°F?
**12.4.5.** Are drums and totes thawed in a heated room at a temperature between 20°C/68°F and 33°C/91°F?
**12.4.6.** After thawing is the oxygen and inhibitor redistributed?

**12.5. In transloading operations, there should be written procedures that describe the response to high temperature, and personnel should be trained on that procedure. This procedure should require PTZ addition when the temperature reaches 45°C/113°F.**

**Records Review**

**12.5.1.** Is there a written procedure describing response to high temperature?
**12.5.2.** Does the procedure call for PTZ addition when the temperature reaches 45°C/113°F?
**12.5.3.** Are personnel trained on that procedure?

## *13.* Controlling Dissolved Oxygen (*refer to AAed4 Section 9 Safe Transport of Acrylic Acid, & Section 7 Bulk Storage Facilities and Accessories* )

Glacial acrylic acid is inhibited with monomethyl ether of hydroquinone (MEHQ). MEHQ stabilizes acrylic acid with respect to polymerization ONLY if dissolved oxygen is present.

**13.1. Transportation containers (T/C, T/T, totes and drums) should contain a blanket atmosphere containing at least 5 volume % oxygen prior to being loaded with acrylic acid. This can be achieved by a gas blending system with the proper controls or by air. Dry, oil-free air is preferred.**

**Records Review**

**13.1.1.** Does the transportation container contain a blanket atmosphere of at least 5% oxygen prior to loading acrylic acid?

**13.2. An inert gas (one containing less than 5 volume % oxygen) should never be used when shipping acrylic acid. Some specific examples where inert gas should never be used include:**

- **Blanket gas in the shipping container**
- **Motive gas for making transfers**
- **Motive gas for blowing lines**
- **Motive gas for pigging lines**
- **Motive gas for clearing lines**
- **Purge gas for shipping containers**
- **Barrier gas for dual seal pumps**

*Any inert gas in contact with acrylic acid can potentially defeat the MEHQ-oxygen inhibitor system.*

**Records review**

Is an inert gas used when shipping acrylic acid in any of the following:
**13.2.1.** Blanket gas in the shipping container
**13.2.2.** Motive gas for making transfers
**13.2.3.** Motive gas for blowing lines
**13.2.4.** Motive gas for pigging lines
**13.2.5.** Motive gas for clearing lines

**13.2.6.** Purge gas for shipping containers
**13.2.7.** Barrier gas for dual seal pumps?

**13.3. In case of inadvertent purging of acrylic acid with an inert gas, the acrylic acid should be sparged with air as soon as possible.**

*Purging of acrylic acid with an inert gas may result in acrylic acid that has no dissolved oxygen, a situation that defeats the MEHQ inhibitor.*

**Records Review**

**13.3.1.** If acrylic acid is inadvertently purged with an inert gas is the acrylic acid sparged with air as soon as possible?

## *14.* Responding to Runaway Polymerization Incidents (*refer to AAed4 Section 11.1 Detection and Response to Incipient Polymerization in a Storage Tank & Section 9 Safe transport of Acrylic Acid)*

**14.1. If at any time during the distribution process, a shipping container is suspected to be undergoing a runaway polymerization, the responsible party (e.g., carrier or customer) should immediately notify CHEMTREC (1-800-424-9300). 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.**

**Records Review**

**14.1.1.** Is CHEMTREC notified whenever a container is suspected to be undergoing a polymerization?

**14.2. PTZ dissolved in a suitable solvent should be stored at each transloading site. PTZ should be added when the container temperature reaches 45°C/113°F. PTZ should be added to the container when a known incompatible contamination has occurred.**

**A. Records Review**

**14.2.1.** Is PTZ stored at the transloading site?
**14.2.2.** Is PTZ added when the container temperature reaches 45°C/113°F?
**14.2.3.** Is PTZ added when a known incompatible contamination has occurred?
**14.2.4.** Has the amount of PTZ or PTZ solution been calculated for container size?

## *15.* Pumps, Piping, Miscellaneous *(refer to AAed4 Section 7.2 Design Considerations & Section 9 Safe Transport of Acrylic Acid)*

Proper design of ancillary systems used during loading/unloading contributes to the safe handling of acrylic acid during shipment. The pumps used to transfer acrylic acid should conform to minimum design standards. Hoses used in conjunction with acrylic acid loading/unloading operations should be designed to minimize the possibility of inadvertent polymerization

**15.1. All pumps and hoses in acrylic acid service should be dedicated to acrylic acid service or properly cleaned prior to use for acrylic acid service. Pumps should be constructed of stainless steel.**

*DOT regulatory requirements call for constant attention during offloading/loading operations.*

**Records Review**

**15.1.1.** Are all pumps and hoses dedicated or properly cleaned prior to use?

**15.1.2.** Are pumps and hoses constructed of proper materials?

**15.2. Steam tracing should never be used on acrylic acid loading/unloading hoses, pipes, or pumps.**

*Steam tracing is not an acceptable choice for freeze protection. There is no way to control the temperature of the steam to be below 35-45°C/95-113°F, the maximum allowable temperature to prevent acrylic acid from freezing or to thaw frozen acrylic acid.*

**Records Review**

**15.2.1.** Is steam tracing used on acrylic acid loading/unloading hoses, pipes or pumps?

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