Acrylic Esters

A Summary of Safety and Handling 4th Edition 2020

Compiled by

Basic Acrylic Monomer Manufacturers, Inc.

Table of Contents

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 Monomers Manufacturers (BAMM) Product Stewardship Committee consists of companies involved in manufacturing and/or marketing of Acrylic Acid and its basic esters (Methyl, Ethyl, Butyl, i-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 acrylates among themselves and with their customers, carriers and other handlers of acrylates. 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 MEHQ (hydroquinone monomethyl ether) inhibited basic esters of acrylic acid, hereafter referred to as acrylates, acrylate esters, or acrylate monomers. The information in this brochure is based on research and experience participating companies in addition to that taken from accompanied references. It is suggested that this entire document along with your safety data sheets (SDSs) be read before using the information provided. In addition, you are strongly encouraged to call your acrylates supplier with any further questions you may have. Additional information on acrylic acid and its basic esters may be found on the BAMM website at http://www.bamm.net.

Acrylates will readily polymerize if not properly inhibited. Even when properly inhibited, polymerization can be caused by contamination or excessive heat, lack of dissolved oxygen or excessive aging. Uncontrolled polymerization can be rapid and very violent, generating large amounts of heat, which may increase pressure. This increase in pressure can cause the ejection of hot flammable vapor and polymer which may auto-ignite.

This brochure is intended to provide essential information to assist personnel who work with acrylates avoid dangerous conditions. Making polymerization prevention features a key part of the design and operation of acrylates storage facilities is an important component in preventing dangerous conditions. The fundamental elements of a well-designed storage system are: redundant temperature monitoring, use of oxygen-containing blanket gas (5 to 21 Vol. -%), and dedicated piping and equipment to prevent contamination. To prevent dangerous conditions, not only a properly designed facility but also safe operating discipline are key to preventing dangerous conditions and health- and property-threatening incidents. 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 ACRYLATES, IN SOME CASES THE PRACTICES OF INDIVIDUAL PRODUCERS MAY DIFFER SLIGHTLY THAN THE GUIDANCE OFFERED IN THIS SUMMARY. IT IS RECOMMENDED THAT USERS OF ACRYLATES, IN DEVELOPING PROCESSES AND PRACTICES FOR HANDLING ACRYLATES, REVIEW INDIVIDUAL PRACTICES DIRECTLY WITH THEIR SUPPLIERS. BAMM AND ITS MEMBER COMPANIES BELIEVE THE INFORMATION CONTAINED IN THIS DOCUMENT IS FACTUAL AND ACCURATE. 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.

2.1 CHEMICAL NAMES

Table 2-1: Names and General Information for Acrylates

Chemical Name	Methyl Acrylate	Ethyl Acrylate	Butyl Acrylate	i-Butyl Acrylate	2-Ethylhexyl Acrylate
IUPAC Name	methyl prop-2-enoate	ethyl prop-2-enoate	butyl prop-2-enoate	2-methylpropyl prop-2-enoate	2-ethylhexyl prop-2-enoate
Synonym	acrylic acid methyl ester; 2-Propenoic acid, methyl ester	acrylic acid ethyl ester; 2-Propenoic acid, ethyl ester	acrylic acid butyl ester; ;2-Propenoic acid, butyl ester; n-butyl Acrylate	acrylic acid isobutyl ester; 2-Propenoic acid, 2-methylpropyl ester; iso-butyl acrylate	acrylic acid ethylhexyl ester; ;2-Propenoic acid, 2-ethylhexyl ester; 1-hexanol, 2-ethyl-, acylate
CAS Number	96-33-3	140-88-5	141-32-2	106-63-8	103-11-7
Molecular Formula	C4H6O2	C5H8O2	C7H12O2	C7H12O2	C11H20O2
Chemical Formula	CH2=CHCOOCH3	CH2=CHCOOC2H5	CH2=CHCOO (CH2)3CH3	CH2=CHCOO CH2CH(CH3)2	CH2=CHCOO CH2CH (C2H5)(CH2)3CH3

2.2 ODOR

The acrylates have very low odor thresholds and may cause discomfort even at low concentrations. Odor threshold concentration ranges, as air dilution threshold values in vol/vol ppb, for the acrylates covered in this guide are given below:

Methyl Acrylate	3-20 ppb
Ethyl Acrylate	0.2-1.3 ppb
Butyl Acrylate	0.9-100 ppb
i-Butyl Acrylate	0.011-0.066 ppb
2-Ethylhexyl Acrylate	16-180 ppb

The odor threshold values shown above represent the full range of available data. Lack of full validation creates some uncertainty in these odor threshold values. To increase the likelihood that your odor avoidance or abatement goals are accomplished, it is suggested that the lowest number in the odor threshold ranges be used for design purposes. Careless handling could also result in releases, which may elicit complaints from neighbors because of the low odor thresholds. In addition, the odor of acrylates warrants judicious selection of methods for waste disposal (*see* Section 10.4).

2.3 REACTIVITY

Properly inhibited, these acrylates are stable under recommended storage conditions. The period of stability decreases with increasing temperature, as the inhibitor is used up more quickly in such circumstances. Higher temperatures may thus cause hazardous polymerization. Contact with strong acids, oxidizing agents, polymerization initiators, heat or flame, sunlight, X-ray or ultraviolet can also lead to hazardous polymerization. (*see* *Appendix A*).

2.4 GLOBAL HARMONIZED SYSTEM FOR CLASSIFICATION AND LABELLING (GHS)

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is an international standard used to classify and communicate hazards of chemicals in a harmonized manner. While toxicological data are not specific to a particular region, regulatory frameworks historically differed significantly between countries and regions. GHS has attempted to standardize hazard communication so that the intended audience (workers, consumers, transport workers, emergency responders, and so forth) can better understand the hazards of the chemicals in use. Under the GHS, substances such as acrylates are classified according to their physical, health, and environmental hazards.

Although the United Nations published and periodically updates the GHS model rule, implementation and interpretation of the standards are determined and enforced regionally or locally. In the EU, GHS was adopted as the CLP regulation (Classification, Labeling and Packaging of Substances and Mixtures) in 2008; in the US, GHS was adopted by the Occupational Safety and Health Administration (OSHA) in 2012 in updates to its Hazard Communication Standard (HazCom), 29 C.F.R. § 1910.1200.

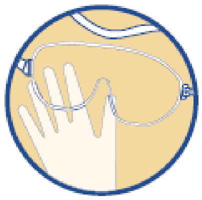
Facilities provide employees access to the suppliers' Safety Data Sheets for chemicals they may be exposed to in a manner regulated by applicable regulations in their jurisdictions. In the US, where OSHA HazCom prescribes how SDS must be kept and provided, each chemical manufacturer and importer independently evaluates and classifies the hazards of its products based upon the information available to them. Although harmonization is a feature of other jurisdictions, such as across the EU under Annex VI to CLP, anti-trust concerns may inhibit companies or trade groups from harmonizing product hazard classifications, at least to the extent that assigning a disparate classification to an otherwise equivalent product may provide a competitive advantage. The latest Safety Data Sheet from the supplier of your product contains the most updated information, and it is recommended to periodically review the SDS and check if an updated version is available.

The BAMM website provides Global Product Summaries and Review documents on each of the acrylates described in this manual. Although BAMM has not classified these products under OSHA HazCom, nor has any legal obligation to do so, examples of such hazard information are publicly available on the BAMM website (http://www.bamm.net/).

3 PROPERTIES AND CHARACTERISTICS OF ACRYLATES

Except where noted, the following physical property values can be found listed on the BAMM website (http://www.bamm.net/)

	Methyl Acrylate	Ethyl Acrylate	Butyl Acrylate	i-Butyl Acrylate	2-Ethylhexyl Acrylate
CAS Number	96-33-3	140-88-5	141-32-2	106-63-8	103-11-7
Appearance	clear, colorless liquid	clear, colorless liquid	clear, colorless liquid	clear, colorless liquid	clear, colorless liquid
Melting Point	-76.5 °C	-71.2 °C	-64.6 °C	-61 °C	-90 °C
Boiling Point (1013 hPa)	80.1 °C	99.8 °C	147 °C	132 °C	215 °C
Relative Density (20 °C)	0.95 g/cm³	0.92 g/cm³	0.9 g/cm³	0.89 g/cm³	0.88 g/cm³
Vapor Pressure	90 hPa at 20 °C	40 hPa at 20.9 °C	5 hPa at 22.5 °C	10 hPa at 25 °C	0.24 hPa at 25 °C
Surface Tension	not surface active	not surface active	not surface active	not surface active	90% saturation at 68.2 mN/m @ 20 °C
Water Solubility	60 g/L at 20 °C	20 g/L at 20 °C	1.7 g/L at 20 °C	1.8 g/L at 25 °C	9.6 mg/L at 25 °C
Partition Coefficient	0.739 at 25 °C	1.18 at 25 °C	2.38 at 25 °C	2.38 at 25 °C	Ca 4 at 25 °C
Flash Point	-2.8 °C	9 °C	37 °C	30 °C	86 °C
Flammability	Highly flammable liquid and vapor	Highly flammable liquid and vapor	Flammable upon ignition	Flammable upon ignition	Not flammable
Explosive Properties	Non-explosive	Non-explosive	Non-explosive	Non-explosive	Non-explosive
Self-Ignition Temperature	468 °C	372 °C	292 °C	350 °C	252 °C
Flammability Limits, in air 25C Lower Limit, vol% Upper Limit, vol%	1.1 14.0	2.5 12	1.3 9.9	1.9 8.0	Vapor pressure at 25°C too low to support combustion
Heat of Polymerization Kcal/mol	18.6	20.2	18.6	16.4	14.4



4 SAFETY AND HANDLING MANAGEMENT SYSTEM

4.1 GENERAL CONSIDERATIONS

Safety and handling training programs are subject to various regulations, which differ depending on the location of the facility. Compliance with such regulations is the responsibility of each company and facility. An example is the OSHA's Hazard Communication Standard (29 C.F.R. § 1910.1200). In addition to legal and regulatory compliance, considering the principles of a Responsible Care Management System® in establishing such programs is also recommended.

Thorough training in the potential hazards, operating procedures, spill and leak prevention techniques, emergency response plans, personal protective equipment, and environmental protection, as relevant, for employees and contractors who handle acrylates helps prevent hazardous conditions and injuries and may be required by regulations. The use of a Safety Data Sheet (SDS), 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 components of a safety and handling program.

Having a qualified multifunctional team plan each step of equipment preparation and cleaning and consider all possible hazards can limit incidents, given the hazardous nature of this job (*see Chapter 8*). Having acrylate facilities be designed by qualified professionals who are aware of the special hazards and industry standards can also improve facility safety (*see Chapter 7*). A one-page safety guide for storage and handling can be found in *Appendix B*.

4.2 SAFETY, HEALTH AND ENVIRONMENTAL REVIEWS

As part of the engineering and construction project for new or modified bulk storage and unloading facilities, having appropriate multifunctional teams conduct risk assessments can improve safety in those facilities. It is suggested that these teams also address commissioning and start-up of the facilities. Your acrylates supplier can provide appropriate SDSs, brochures, and other information. The Acrylate Audit and Assessment Protocol in *Appendix F* will assist your team with this process.

A typical review team utilizes expertise from operations; engineering; construction; technology; and safety, health, and environmental functions. Such multifunctional teams typically discuss the potential hazards, as well as accident prevention and emergency response, and keep appropriate documentation. It is recommended that the multifunctional teams also address odor control. Documenting EHS (Environmental, Health and Safety) reviews and making them subject to the management of change process developed for your facility is also recommended.

4.3 WRITTEN OPERATING PROCEDURES

Providing stepwise directions in written operating procedures to employees and contractors involved in handling acrylates helps improve clarity and safety. Typically, such procedures are 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 to provide all responsible personnel with documented training on operating procedures (*see Section 4.4*).

Having a management-of-change program in place helps ensure that all changes are properly reviewed and documented before implementation.

4.4 DOCUMENTED TRAINING PROGRAM

Thorough training in the potential hazards, operating procedures, spill and leak prevention techniques, emergency response plans, personal protective equipment, and environmental protection, as relevant, for employees and contractors who handle acrylates helps prevent hazardous conditions and injuries. Legally required training components are provided by relevant regulations, e.g., OSHA regulations in the United States (29 C.F.R. § 1910 Subpart H). Documented training helps maintain a good safety, health, and environmental program. Generally, an effective training program ensures that new personnel are adequately trained for their job duties and that changes are communicated to those affected. Such programs can be strengthened by promoting awareness of safety, health, and environmental issues, providing affected personnel the opportunity to make suggestions, and thoroughly reviewing accidents.

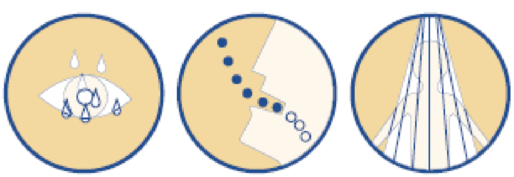
Regularly held meetings which cover safety, health, and environmental issues are typically a major part of training programs. In such meetings, related hazards, incidents, and suggestions are periodically reviewed and attendance is documented.

4.5 WRITTEN EMERGENCY RESPONSE PLANS

Written emergency response plans are recommended for potential spills, fires and inadvertent polymerizations (*see* Chapter 11). These emergency response plans are written by qualified personnel and typically reviewed by a multifunctional team. Your acrylates supplier may be able to provide additional information.

Periodic review of and updates to the written emergency response plans by a multifunctional team help keep such plans up-to-date. Including these emergency response plans in safety, health, and environmental reviews and making them part of the documented training program ensures personnel is aware of these plans . Documented drills are also suggested as part of the emergency training program.

Addressing corrective action and communication in the written emergency response plans is highly recommended. 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 (or in Canada CANUTEC at 888-226-8832). CHEMTREC (or CANUTEC) 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 (or CANUTEC) is normally contacted if a transport vessel is involved.



5 HEALTH AND SAFETY INFORMATION

5.1 TOXICOLOGY

This section is drawn from the Acrylate Category Review (as of publication of this manual, the review was last updated 5/7/2012) prepared by BAMM and posted on the BAMM website (http://www.bamm.net). Please refer directly to the website for detailed information on individual acrylates.

5.1.1 Physicochemical Properties

Acrylates are clear, colorless liquids which have a characteristic unpleasant odor and high chemical reactivity.

The vapor pressure, water solubility, and density of the esters decrease with increasing chain length and molecular weight. They have moderate to low solubility in water with values ranging from 60 g/l

(Methyl Acrylate) to 9.6 mg/L (2-Ethylhexyl Acrylate). The vapor pressure values at room temperature range from 90 hPa (methyl acrylate) to 0.24 hPa (2-Ethylhexyl Acrylate).

5.1.2 Human Health Effects

Available studies suggest that acrylates are generally of low to moderate toxicity but are moderate to strong irritants. The irritancy of the esters tends to decrease with increasing molecular weight. The esters can cause skin allergies. Most of the effects seen in animal studies are associated with the irritancy of the chemical. Animal studies do not indicate long-term target organ effects.

5.1.2.1 Acute Toxicity

Acrylates are harmful if swallowed. The dermal and inhalation lethality values (LD_{50} or LC_{50}) indicate a moderate to low order of toxicity. Concentration-dependent irritation at the site of contact can occur for all routes of exposure. The acute toxicity of the esters generally decreases with increasing ester carbon chain length.

5.1.2.2 Irritation/Sensitization

Acrylates are strong to moderate irritants. Esters exhibit a low but definable potential for dermal sensitization. If inhaled, acrylate vapors can also cause irritation to the mucous membranes of the respiratory tract.

5.1.2.3 Repeated Dose Toxicity

The acrylates demonstrate similar toxicity profiles in rats and mice via inhalation, dietary and/or dermal routes of administration in tests ranging from 28 days to 2 years. No evidence of systemic toxicity was observed; effects seen in these studies are consistent with direct irritation effects.

5.1.2.4 Genetic Toxicity

Extensive genetic toxicity testing of acrylates indicates a lack of potential for genetic toxicity in both in vitro (test tube) and in vivo (live animal) tests.

5.1.2.5 Developmental/Reproductive Toxicity

Acrylates have been tested for developmental toxicity in at least one species via oral administration or inhalation. Neither evidence of fetotoxicity nor birth defects were seen at dose levels which did not cause maternal toxicity.

Subchronic and chronic testing indicates no effects on reproductive organs.

5.1.2.6 Carcinogenicity

Acrylates have been assessed for carcinogenicity in a number of studies by various routes of exposure and found in most studies to be not carcinogenic. For MA, EA and 2EHA, in isolated studies, treatment of rodents with very high, corrosive doses produced tumors at the site of contact. These artificial laboratory conditions have no relation to real-world use of the acrylates–humans simply would not have such exposures, and the evidence strongly indicates the observed tumors are not relevant for evaluating human cancer potential.

5.1.2.7 Toxicokinetics

All available evidence indicates acrylates are rapidly metabolized and do not accumulate in the mammalian body. Acrylate esters were found to disappear rapidly in rat whole blood *in vitro*.

Ethyl Acrylate disappeared in tissue homogenates *in vitro*; the rate of hydrolysis was ~20 times greater in liver homogenates than in kidney or lung homogenates. Similar results were obtained for Methyl Acrylate. The rate of hydrolysis in rat liver homogenates increased in the order Butyl < Ethyl < Methyl. Disappearance of the acrylate esters *in vitro* in tissue homogenates, but not in blood, was quantitatively associated with the appearance of acrylic acid, indicating that the esters hydrolyze to the acid and the associated alcohol.

5.2 INDUSTRIAL HYGIENE

5.2.1 General

At this time, the American Conference of Governmental Industrial Hygienists (ACGIH) has adopted official Threshold Limit Values (TLVs®) of 2, 5 and 2 ppm, 8-hour time-weighted averages for Methyl, Ethyl and Butyl Acrylates, respectively, with skin notations for Methyl Acrylate. The ACGIH further recommends a 15 ppm maximum short-term exposure limit (STEL) for Ethyl Acrylate.

Specific exposure limits differ per jurisdiction. In the US, OSHA has established standards of 10, 5 and 10 ppm, 8-hour time-weighted averages for Methyl, Ethyl and Butyl Acrylates, respectively, with skin notations for Methyl and Ethyl Acrylates. OSHA also has a 15-minute STEL of 25 ppm for Ethyl Acrylate. No standards have been established by the ACGIH or OSHA for i-Butyl Acrylate or 2-Ethylhexyl Acrylate. Refer to your supplier's SDS or contact your supplier for up to date guidance. Supplied air respirators or self-contained breathing apparatus (SCBA) approved by the National Institute for Occupational Safety and Health (NIOSH) are indicated for use in case of an emergency when exposures to high concentrations of acrylate may occur. Air purifying respirators with organic vapor cartridges may be satisfactory for exposure to low level concentrations.

To prevent excessive exposure, handle acrylates in well ventilated places or in completely closed systems (that is, with no potential for human exposure). In the event of a release of an acrylate, the standard procedure is to evacuate an area immediately and have only properly trained personnel equipped with appropriate safety equipment enter. It is advisable to have several sets of safety equipment available at all times, stored outside of, but near, the area where the acrylates are used. Full protective clothing (*see Section 5.5*) is almost always worn for work involving line breaking or entering into an acrylate system to prevent exposures that could cause skin or other irritation.

5.2.2 Personal Hygiene

The following are generally recommended personal hygiene measures; each facility is responsible for compliance with applicable regulations on personal hygiene measures and equipment. Warning workers to avoid breathing acrylate vapors protects their health and safety. Appropriate respiratory protection is typically used when exposure to acrylate vapors or mists may occur. Worker' familiarity with the location and operation of respiratory protective equipment will enable them to quickly access such equipment when needed. Instruction of workers to immediately report any incident in which an acrylate vapor was inhaled enables immediate treatment. Location of safety showers and eyewash facilities in close proximity to where acrylates are being handled enables prompt washing of exposed skins or eyes with copious amounts of water. To prevent further exposure: immediately remove all contaminated clothing and footwear. properly dispose of contaminated shoes and other leather items; and properly decontaminate (launder) all contaminated clothing before reuse. Under no circumstances should contaminated clothing be taken home for laundering. Where decontamination is not feasible, properly dispose of clothing.

5.3 MEDICAL MANAGEMENT

Having medical management determine an employee's fitness to work with or around acrylates ensures only fit employees handle such chemicals. Establishing procedures to be followed if an exposure incident occurs improves response time and limits any injuries.

Typically, workers are evaluated prior to working in a chemical environment. This evaluation generally includes vision testing and respiratory clearance. Confirmation of overall fitness helps ensure that the employees are able to safely perform the jobs for which they are being hired.

Contact lenses are not recommended for use in areas where there is a potential for exposure to acrylates. Please see Sections 5.1 on acute exposure and 5.5 on eye protection for assistance in developing policies and procedures. Since the use of respiratory protection may be required by regulation in the work area, evaluating respiratory fitness regularly to determine the employees' ability to wear a respirator helps ensure compliance and worker safety.

5.4 FIRST AID

5.4.1 General

It is generally recommended for every employee working in a potentially dangerous environment (with chemicals, machinery, etc.) to 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 the person providing assistance. Employees typically know the location of all emergency eyewash stations and showers. Having the phone number(s) to call for emergency medical services and all workplace-specific emergency procedures readily accessible helps reduce response times.

When providing first aid to a person who has been exposed to acrylates, removing the victim from the area prevents further exposure after decontamination. Determining the type of exposure the person has experienced– eye or skin contact, inhalation or ingestion – helps identify the appropriate care. If possible, avoid leaving an injured person alone to ensure someone is available to assist the injured person. If feasible, instructing a co-worker to call for help while assistance is being provided to the affected individual improves care. Generally, AVOID INDUCING EMESIS (VOMITING) because of the potential for rapid onset of CNS depression or seizures with possible aspiration of gastric contents. Cautious gastric lavage followed by administration of activated charcoal may be of benefit if the patient is seen soon after the exposure.

In the event of an accidental exposure to acrylates while working alone, leaving the area prevents the worker from being further exposed. After calling a co-worker for help, following procedures to remove or dilute contamination on the exposed worker prevents continued exposure. Basic first aid procedures for acrylates exposure are given in 5.4.2 through 5.4.5.

5.4.2 Contact with Eyes

In case of eye exposure to acrylates at any concentration, to remove the acrylate, immediately flush eyes with water at the nearest eyewash station for at least 15 minutes, while occasionally lifting the lower and upper lids open and away from the eyes. Evaluation of the exposed individual by a physician as soon as possible reduces the potential for serious harm. If a physician is not immediately available, continuing the process of flushing the eyes with water for a second 15-minute period can also reduce the potential for harm.

5.4.3 Contact with Skin

If acrylates come in contact with a person's skin or clothing, to remove the acrylate, rinse off in the nearest safety shower. Once under the shower, removing all contaminated clothing, jewelry and shoes enables thorough cleaning. Washing the affected area(s) of the person continuously with large quantities of water for at least 15 minutes or longer if acrylate odor persists helps ensure full decontamination. Evaluation of the exposed individual by a physician as soon as possible reduces the potential for serious harm, including dermal burns and hypersensitivity reactions. Avoiding application of ointments or medications to the skin without specific instruction from a physician helps prevent potential unintended harm.

TO PREVENT FURTHER EXPOSURE: APPROPRIATELY DE-CONTAMINATE ALL CONTAMINATED CLOTHING PRIOR TO RE-USE. DO NOT TAKE CONTAMINATED ITEMS HOME FOR LAUNDERING! IF THE FACILITY IS NOT EQUIPPED TO DECONTAMINATE CLOTHING AND OTHER ITEMS, PROPERLY DISPOSE OF AND REPLACE THEM. CONTAMINATED LEATHER ITEMS CANNOT BE ADEQUATELY DECONTAMINATED AND ARE DISCARDED TO PREVENT FURTHER EXPOSURE.

5.4.4 Inhalation

If acrylate vapors are inhaled, immediately removing the affected person from the contaminated area to a well-ventilated area prevents further exposure. Evaluation of the exposed individual by a physician as soon as possible reduces the potential for serious harm, including acute lung injury, and significant respiratory tract irritation. If available, administering humidified air as first aid for persons who have inhaled acrylates reduces irritation symptoms. Oxygen may be administered if indicated by evidence of poor oxygenation status, such as increased respiratory rate, cyanosis or decreased O_2 saturation by pulse oximetry, but to ensure proper administration, avoid provision by untrained individuals– wait for emergency medical assistance.

5.4.4.1 Suggestions to Physicians

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

In most exposures, administration of oxygen at atmospheric pressure has been found to be adequate. This is best accomplished by use of a face mask with a reservoir bag of the non-rebreathing type. Inhalation of pure oxygen (100 percent) is generally limited to one hour of continuous treatment to avoid harm to the lungs. After each hour, therapy may be interrupted. It may be reinstituted as the clinical condition indicates.

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

IT MAY NOT BE ADVISABLE TO ADMINISTER OXYGEN UNDER POSITIVE PRESSURE IN THE PRESENCE OF IMPENDING OR EXISTING CARDIOVASCULAR FAILURE.

Inhaled beta-2 adrenergic agonists can be administered, if available, if bronchospasm develops. Systemic corticosteroids may be used in patients with significant bronchospasm. It is not clear from the published literature that administration of systemic corticosteroids early following inhalation exposure to respiratory irritant substances can prevent the development of noncardiogenic pulmonary edema. The decision to administer or withhold corticosteroids in this setting is currently made on clinical grounds.

5.4.5 Ingestion

If no respiratory compromise is present, ingestion of any quantity of acrylates can be treated by having the person drink milk or water as soon as possible after ingestion to dilute the acrylate. Dilution may only be helpful if performed in the first seconds to minutes after ingestion. The ideal amount is unknown; no more than 8 ounces (240 mL) in adults and 4 ounces (120 mL) in children is recommended to minimize the risk of vomiting (drinking large quantities of water could actually induce vomiting). **AVOID INDUCING VOMITING TO PREVENT INJURY.** Vomiting can potentially cause burns to the esophagus and other internal organs. To obtain medical assistance, immediately contact local emergency medical services or the local poison control center. Evaluation of the exposed individual by a physician as soon as possible reduces the potential for serious harm.

5.5 PERSONAL PROTECTIVE EQUIPMENT

5.5.1 General

The following are generally recommended personal protective equipment (PPE) measures; each facility is responsible for compliance with applicable PPE regulations. In the US, OSHA regulates the selection and use of PPE in 29 C.F.R. part 1910, Subpart I, §§ 1910.132-.138, and Appendices A and B. Full protective clothing is typically used, as follows: a chemical resistant splash suit, gloves, boots, eye protection, hard hat and respiratory protection. PPE is selected based on the potential for exposure to a particular chemical(s), and the unique properties of that chemical. In general, PPE is not an adequate substitute for appropriate workplace controls (such as ventilation) and other safe work practices. There may be situations when the only practical means of preventing employee exposure is through the effective use of PPE. Selecting personal protective equipment[9,10] on the basis of potential exposure ensures proper levels of safety. When PPE is provided to employees, providing training in how, where, when, and why the equipment is to be used helps ensure proper use and prevent injuries. A facility that has PPE on site generally also has provisions for decontaminating and replacing such equipment as necessary.

5.5.2 *Eye Protection*

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

5.5.3 *Skin Protection*

Skin protection may be found in many forms. Hand protection, such as chemical resistant gloves, protective arm sleeves, aprons, full body coveralls, boots, and head coverings are among the types available. Skin protection for use with acrylates is made of a material impervious to acrylates to prevent exposure through permeation. Butyl rubber of 0.4 to 0.6 mm (15.7 to 23.6 mils) thickness is a good example; nitrile could be acceptable for short-duration tasks. Polyethylene-polyvinyl alcohol laminate gloves (0.08mm, 3 mils) were found to offer the greatest level of protection against acrylates in a 1999 study of chemical-resistant gloves sponsored by BAMM.[11] 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 acrylate permeation into the safety shoe.

Skin protection PPE is available in a variety of sizes and ensuring it is available in a size that fits the employee wearing it helps maximize protection; improperly sized PPE may compromise its effectiveness and create additional safety hazards. When skin protection PPE is used, a means of cleaning or disposal/replacement of the PPE is normally available to ensure safety and effectiveness of PPE. In the event of permeation, gloves and other PPE should be replaced, and the chemically-contacted materials properly disposed of as a contaminated waste.

5.5.4 *Respiratory Protection*

Respiratory protection is available in two basic varieties: air purifying, and air supplied. In general, air purifying respirators (fitted with organic vapor cartridges) provide less protection than air supplied respirators. Both types, however, have their particular advantages and limitations. The appropriate type of respirator is selected to provide the appropriate level of protection for the anticipated degree of exposure to airborne acrylates (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 used in the US is approved by NIOSH. Regulations typically require respirators to be carefully maintained, inspected, and cleaned; facilities are responsible to ensure compliance with all applicable regulations. All employees required to wear respiratory protection are typically medically cleared to do so, to ensure 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 C.F.R. § 1910.134.

5.5.5 *Head Protection*

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

6 INSTABILITY AND REACTIVITY HAZARDS

6.1 UNINTENDED POLYMERIZATION

One of the prevailing characteristics of acrylates is their high reactivity in the presence of free radicals. Free radicals can be generated by heat, light (UV) or irradiation of X-rays and by activation of radical forming materials.

Many substances are known to readily promote polymerization, such as peroxides, peroxide forming and other free radical forming compounds (aldehydes, amines, azides, ethers, nitric acid). Redox-reactions of polyvalent heavy metal ions or hydrolysis of metals with strong mineral acids may likewise initiate polymerization. Moisture enhances the likelihood of polymerization.

There are seven main causes of unintended polymerization of acrylates:

- overheating (especially local overheating),
- photo-initiation,
- contamination,
- corrosion,
- inhibitor depletion,
- inhibitor deactivation (e.g. via dissolved oxygen depletion), and
- aging beyond shelf-life.

If procedures for proper and safe handling are not regarded, runaway polymerizations may occur. Depending on external conditions, the polymerization can proceed with moderate speed, or under unfavorable conditions, with increased pressure and heat release.

An explosion hazard may also exist if large clouds of vapor escape from the storage container (e.g. due to the heat of polymerization). If the container is poorly vented, pressure build-up may occur rapidly and can lead to rupture of the vessel. High temperatures caused by a runaway reaction can pose a serious risk of the reacting mass self-igniting. (*See Section 11.1 Detection and Response to Incipient Polymerization in a Storage Tank).*

Acrylates are commonly stabilized with 10 to 20 ppm MEHQ (monomethyl ether of hydroquinone or p-methoxyphenol) to ensure protection from an untimely polymerization. This stabilization inhibitor requires oxygen to perform its function. This protection is only effective at moderate ambient temperatures and for handling conditions described in the following chapters. MEHQ functions by scavenging free radicals which may otherwise cause polymerization, as depicted in the following:

$$AE + R\bullet \longrightarrow R-AE\bullet$$
$$R-AE\bullet + O_2 \longrightarrow R-AE-O_2\bullet$$
$$R-AE-O_2\bullet + MeHQ \longrightarrow R-AE-O_2-MeHQ\bullet$$
$$R-AE-O_2\bullet + R-AE-O_2-MeHQ\bullet \longrightarrow Saturated-Quinone$$

Maintaining a head space containing sufficient oxygenated air above the acrylate ensures inhibitor effectiveness. Handling acrylates under an inert atmosphere is dangerous due to potential oxygen depletion.

6.1.1 Overheating

Most commercially available grades of acrylates have a shelf life of 1 year if properly handled, but some may have a shorter shelf life. Your supplier can provide additional information, and it is recommended to monitor the age of the product. Shelf life is reduced with increasing temperature. Common practice is to maintain acrylates at ambient temperatures (no heating or cooling). Recommended storage temperatures are typically below 35-40˚C. Your producer can provide specific product recommendations. Due to their physical properties, acrylates do not need to be heated for transport or storage.

Where it may be desired to heat the material, it is important to protect against local overheating. DO NOT USE STEAM but consider using a tempered water system limited to 45˚C. Testing and experience at these temperatures have shown no impact on safety, as long as shelf life is not exceeded. Avoiding overheating, especially local overheating of acrylates that may not be detected by temperature sensors, is important to avoid unintended polymerization. Overheating may occur if, for example, pumps are circulating without temperature monitoring of the circulated product, or steam is being applied to pipe surfaces accidentally or intentionally.

6.1.2 Photo-Initiation by UV light and X-ray radiation

Acrylates can polymerize as a result of photo-initiation. Where sight glasses or other transparent sections are needed for visual observation in acrylates service, covers to exclude light between observations can avoid photo-initiated polymerization. Storing esters only in containers designed to be impermeable to UV light and avoiding placement of containers such as IBCs, drums, bottles etc. in direct sunlight or UV radiation also avoids such polymerization.

Exposure of acrylates to direct sun, UV or X-ray radiation is normally avoided to prevent unintended polymerization.

However, under some circumstance's cargo can be inspected safely with X-rays. Prior evaluations have been done using mobile scanners with an energy dose of 0.03 mSv for a single scan. The level of X-ray energy absorbed by acrylates for such inspections, using mobile X-ray scanners, is far below the level that could alter the shelf life recommendations of acrylates.

6.1.3 Contamination

Exercising good housekeeping helps avoid contamination of acrylates, which can result in polymerization. Many compounds can promote polymerization, such as:

- Peroxides;
- Compounds which form peroxides and free radicals such as azo compounds, azides, etc.;
- Initiating radicals may also be formed under certain conditions from polyvalent heavy metal ions participating in redox reactions. Such metal ions include: copper, cobalt, nickel, chromium and iron;
- Nitric acid present, even in small amounts can also start polymerization;
- The presence of iron or rust may cause polymerization in some circumstances.

See Appendix A for a more detailed list.

Protecting tanks from mistakenly being charged with other materials or from back flow from other production vessels avoids contamination. This can be best achieved by using dedicated loading and unloading lines with proper identification. As the polymer can act as a seed for further polymerization, inspecting tanks, piping and transport vessels periodically for polymer formation also helps avoid unintended polymerization. Polymers of the esters are commonly soluble in the monomer.

Some contaminants can cause polymerization by initiating polymerization, consuming inhibitor or by consuming dissolved oxygen. This can be easily detected and filtered. A list of incompatible materials is indicated in *Appendix A*.

Dedicated lines and unloading equipment, including hoses, pumps, transfer lines etc., are the recommended way to avoid cross-contamination with incompatible materials.

6.1.4 Inhibitor Depletion

Inhibitors (stabilizers) are depleted with time. Elevated temperatures will accelerate this process. Observation of the recommended storage time and temperature can help prevent depletion of the inhibitor as well as premature depletion of oxygen. Elevated temperatures can accelerate inhibitor depletion and cause excessive peroxide buildup.

6.1.5 Inhibitor Deactivation/Oxygen Depletion

Dissolved oxygen is essential for the effective functioning of MEHQ. Once the dissolved oxygen is consumed, polymerization will start.

If oxygen depletion is suspected, replenishing oxygen allows for the continued functioning of the stabilizer *(see Section 7.2.2)*. Oxygenation can be accomplished by thoroughly aerating the liquid phase, (e.g., recirculation of the inventory in tanks or agitating drums by rotating). Maintaining a head space containing sufficient oxygen above the monomer ensures inhibitor effectiveness.

To avoid an unintended polymerization, never create an inert atmosphere above an acrylate. Oxygen levels at 5 Vol.-% in the gaseous atmosphere ensure that the inhibitor remains effective.

Most acrylates, such as Methyl Acrylate and Ethyl Acrylate (see Chart 3.1.1) are flammable. Standard industry handling practice for most flammables is to use an inert gas (nitrogen) for blowing and pigging of lines for pressure drop type level measurement devices, and for blanketing of tanks. However, the MEHQ inhibitor used in acrylates requires the presence of dissolved oxygen in the monomer. Nitrogen or an oxygen depleting gas therefore are not used in handling acrylates.

In some applications (e.g. where tank vents are collected into a header for incineration) there may be safety concerns that prevent the use of air to blanket flammable acrylates. It is recommended to perform an appropriate safety analysis and consult applicable local regulations. The limiting oxygen concentration (LOC) is the minimum concentration of oxygen that will propagate a flame in a gas mixture. The LOCs of Methyl Acrylate and Ethyl Acrylate are approximately 8.5 and 9.0 respectively. Flammable acrylates can be kept in contact with an air-nitrogen mixture containing 5 to 8 Vol.-% oxygen to avoid flammability concerns during storage while allowing the inhibitor to function properly. Other options include the use of flame arrestors in piping connections to the storage vessel (see Section 7.2.9). Flame arrestors may plug over time. When using flame arrestors, having proper preventative maintenance programs in place helps prevent or detect pluggage before the system becomes plugged.

An air-nitrogen mixing station can be designed to yield a gas containing a minimum of 5 Vol.-% oxygen; please refer to *Section 7.2.9.1*. Carefully considering equipment measurement tolerances ensures that the operating range remains comfortably between the LOC and the minimum recommended oxygen concentration (5 Vol.-%). For example, if analysis of the proposed mixing station design shows that the tolerance is 1.5, then the set point of the system would be 6.5 Vol.-% to ensure that the oxygen concentration is always above 5 Vol.-%. Reviewing the design of the mixing station with local safety personnel can ensure that it meets the criterion for both protection from flammability of the material and for protection from unexpected polymerization through all normal and emergency operations.

MEHQ will be depleted slowly over time of storage. To evaluate how much remains, the concentration of active MEHQ can be analyzed with a chromatographic separation technique but not a photometric analytical technique, as the latter does not distinguish between active and inactive quinone components.

6.1.6 Polymerization Detection

A temperature rise that cannot be related to an external heat source typically is considered an indication of a runaway polymerization. While exercising caution, if a sample can be safely acquired, it can be used to test for the presence of soluble polymer to confirm polymerization. While the presence of soluble polymer confirms an ongoing polymerization, a negative result is not conclusive until all the other indicators (which may include multiple samples) indicate there is no polymerization. To test for polymer in the monomer, add 20 ml of the monomer to 80 ml of methanol. The polymer is insoluble in the methanol and the mixture will be cloudy if there is any polymer present. A simple temperature rise may indicate an ongoing polymerization. In the case of a slow temperature rise and with note of the caution below, the presence of soluble polymer in the monomer is one way to verify that a polymerization is under way before temperature extremes are reached. (*See Chapter 11*).

Even slow polymerization has the potential to accelerate into a runaway reaction. If the temperature rises above 45°C or the rate of rise is greater than 2°C per hour, and no source of external heat has been identified, this is typically considered the onset of polymerization. If the temperature rises at a rate greater than 5°C per hour or the temperature reaches 50°C, the situation is critical; see *Chapter 11*.

6.2 HIGH TEMPERATURE COMPOSITION

In unvented containers or containers whose vent has plugged, high temperatures and pressures can build up over time. Small vents especially can plug easily, because of slow polymerization of condensed monomer vapors which are likely to be uninhibited. At very high temperatures, >180˚C, Acrylic Esters will undergo degradation, e.g. decarboxylation. With a decomposition reaction, very high pressures can be generated in a vessel. Rupture of the vessel is possible

In the event of an unintended polymerization in a vessel, high pressures may persist long after the polymerization event is over, because of plugging of the vent lines and the presence of decomposition gases.

6.3 FLAMMABILITY

According to the UN Globally Harmonized Standard for Classification and Labeling (GHS), Ethyl and Methyl Acrylates are classified as Flammable Liquid 2 (H 225, highly flammable liquid and vapor); Butyl and i-Butyl Acrylate are classified as Flammable Liquid 3 (H 226, flammable liquid and vapor); and 2-Ethylhexyl Acrylate is classified as a Flammable Liquid 4 (H 227, combustible liquid).

According to the US-based National Fire Protection Association (NFPA), Methyl and Ethyl Acrylates are Class IB flammable liquids (NFPA 30) and i-Butyl Acrylate is a Class IC flammable liquid (NFPA 30). Methyl Acrylate, Ethyl Acrylate and i-Butyl Acrylate are also given a flammability rating of 3 (NFPA 704). Butyl Acrylate and 2-Ethylhexyl Acrylate are classed as combustible liquids by NFPA and are given flammability ratings of 2.

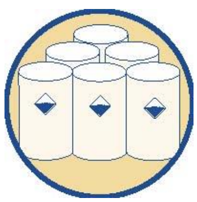
US Department of Transportation (DOT) Hazardous Material Transportation regulations require the posting of "FLAMMABLE LIQUID" labels on shipping containers and "FLAMMABLE" placards on vehicles for Methyl, Ethyl, Butyl and i-Butyl Acrylates. 2-Ethylhexyl Acrylate requires a "COMBUSTIBLE" placard on vehicles.

The installation of flame arresters on tanks holding flammable liquids may be required by federal, state or local ordinance or by insurance companies. For increased safety, flame arresters may be installed in any vapor (vent) line which can be opened directly to the atmosphere, with the exception of the emergency vent. When using closed circuit unloading, it is recommended to install an additional flame arrester in the vapor line. Inspecting flame arresters at least once every six months for blockage by polymer helps ensure proper operation.

Electrical installations in Class I hazardous locations, as defined in Article 500 of the National Electrical Code, are usually installed in accordance with Article 501 of the Code. Ensuring electrical equipment is suitable for use in atmospheres containing acrylate vapors reduces combustion risk. See Flammable and Combustible Liquids Code (NFPA 30), National Electrical Code (NFPA 70), Static Electricity (NFPA 77) and Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids (NFPA 325M). Additionally, electric installations may be subject to other federal, state, or local requirements.

Owners and operator are responsible to ensure all installations and procedures conform to federal, state and local ordinances and the requirements imposed by underwriters and insurance companies. Although information in this section pertains primarily to the US, different requirements apply in different countries.

Substance	GHS	GHS	NFPA	NFPA	DOT
Methyl Acrylate	Flammable Liquid 2	H225, Highly Flammable Liquid and Vapor	Class 1B Flammable Liquid	3	Flammable Liquid
Ethyl Acrylate	Flammable Liquid 2	H225, Highly Flammable Liquid and Vapor	Class 1B Flammable Liquid	3	Flammable Liquid
Butyl Acrylate	Flammable Liquid 3	H226, Flammable Liquid and Vapor		2	Flammable Liquid
Isobutyl Acrylate	Flammable Liquid 3	H226, Flammable Liquid and Vapor	Class 1C Flammable Liquid	3	Flammable Liquid
2 Ethylhexyl Acrylate	Flammable Liquid 4	H227, Combustible Liquid		2	Combustible Liquid (>119 gals)



7 BULK STORAGE FACILITIES AND ACCESSORIES

7.1 GENERAL CONSIDERATIONS

Ideally, acrylates or acrylic esters are stored at ambient temperature (i.e., no heating or cooling). Recommended storage temperatures are typically below 35-40˚C but may vary based upon local ambient conditions and specific product specifications. It is important to check with your producer for specific product recommendations. These recommended storage temperatures are established to avoid nuisance alarms yet allow for time to detect and react to a potential inadvertent polymerization.

The most common tank design follows the American Petroleum Institute (API) standards. This design incorporates a vertical shell, a flat bottom and a conical top. Tanks can be constructed of steel, baked phenolic-lined steel or stainless steel. Steel tanks are the most common because of cost considerations. Tanks are usually set on a concrete pad within a concrete dike of sufficient capacity and have a tank well with a bottom drain line to allow complete tank drainage. Alternate tank designs may be acceptable, and you may consider reviewing any alternative tank configurations with your supplier. Tanks used in acrylate service are sometimes painted white to minimize heat absorption. Tanks are well grounded electrically, with the electrical resistance between the tank and ground not exceeding 5 ohms.

The optimum capacity of an acrylate storage tank is a function of the transportation mode, the expected consumption rate, the expected frequency of deliveries and the monomer shelf life. For the most efficient scheduling of truck deliveries, storage tanks are generally at least 1.5 times the volume of the expected delivery.

Adequate inhibition avoids polymerization when storing acrylates. The standard inhibitor concentration of commercial acrylates is 10-20 ppm MEHQ. Phenolic inhibitors (stabilizers) like MEHQ require the presence of dissolved oxygen to function (*see* *Section 7.2.9.1*). Therefore, to avoid polymerization, an atmosphere containing 5 to 21 Vol.-% of oxygen is maintained above the acrylate. **NEVER USE AN "INERT" (OXYGEN-FREE) ATMOSPHERE.** Typically, a 10% void volume in acrylate bulk storage vessels is used as a buffer against tank overflow. This also provides adequate oxygen containing gas to activate the MEHQ inhibitor. In addition, acrylates are hygroscopic. A means of excluding moisture in the atmosphere may be provided to prevent contamination of the monomer. Higher concentrations of water which lead to the formation of an aqueous phase may cause polymer formation.

Methyl , Ethyl and i-Butyl Acrylates readily form, and Butyl Acrylate may form, flammable mixtures with air at ambient temperatures. The risk of flammability can be further minimized by reducing the oxygen content in the atmosphere (to not less than 5 Vol.-% to ensure inhibitor functioning). Therefore, it is recommended that flame arresters be considered and precautions— such as proper bonding and grounding of components (such as dip pipes), avoiding free falling, splashing or spraying liquid and limiting initial fill velocity of tanks—be taken to minimize the risk of static discharge and other potential sources of ignition (*see Section 7.2.14*). The risk of flammability can be further minimized by reducing the oxygen content in the atmosphere (to not less than 5 Vol.-%) or in some cases, by reducing the monomer temperature to lower the vapor pressure. **ALWAYS ENSURE THAT THE ATMOSPHERE ABOVE THE ACRYLATE CONTAINS AT LEAST 5% OXYGEN BY VOLUME**. In lean gas systems, the use of technical protections can ensure the oxygen concentration does not get too low or too high.

Avoiding condensation in vent lines and nozzles helps avoid unintended polymerization and plugging. Condensed acrylates can quickly polymerize due to a lack of inhibitor. Sloping vent lines allows for drainage whenever possible. **POLYMERIZATION IN VENT SYSTEMS CAN LEAD TO DANGEROUS PLUGGING AND THE FAILURE OF PRESSURE OR VACUUM RELIEF SYSTEMS.**

Keeping acrylates free of contamination, by using dedicated equipment and lines, for example, can avoid unintended polymerization. EVEN TRACE CONTAMINATION WITH AN INITIATOR CAN LEAD TO A DANGEROUS POLYMERIZATION (*see Section 6.1.3*).

Carefully reviewing the design of all vessels and accessories for potential hazards prior to storing or handling acrylates in a facility helps ensure safety (*see Section 7.2*). **STORAGE IN A VESSEL WHERE STEAM CAN ACCIDENTALLY HEAT THE MATERIAL DIRECTLY THROUGH A HEAT TRANSFER SURFACE OR BY DIRECT ADDITION TO THE VESSEL CAN LEAD TO DANGEROUS POLYMERIZATION.** Storage in process vessels or in storage tanks designed for other chemicals can also lead to unsafe conditions.

A HIGH TEMPERATURE ALARM ON ALL ACRYLATE STORAGE VESSELS (INCLUDING CHARGE OR WEIGH TANKS) IS RECOMMENDED . 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.

PROTECTION FROM OVERHEATING IN ALL ACRYLATE PUMPS THAT COULD POTENTIALLY OVERHEAT IF DEADHEADED (BLOCKED IN) CAN AVOID DANGEROUS POLYMERIZATION. 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.

Periodic inspection of vent nozzles and lines for polymer, and prompt removal of any polymer found in the system, avoids potential unintended polymerization. Polymer can cause plugging and may promote further polymerization under some conditions. It is generally considered good practice not to leave stagnant lines or nozzles liquid-full for extended periods. Dissolved oxygen is slowly consumed and is typically 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.

Acrylate vapors are highly odorous even at very low concentrations. At higher concentrations, acrylate vapors can create health and flammability hazards (see Sections 5.1.1 and 6.3). **MINIMIZING ODORS BY HAVING WELL-MAINTAINED CONTROL DEVICES IN PLACE AND BY FOLLOWING GOOD OPERATING PROCEDURES HELPS AVOID SUCH HAZARDS.** Keeping indoor acrylate storage facilities well ventilated prevents local accumulation of vapors.

7.1.1 *Odor Control*

Odor control techniques are a primary part of storing and handling acrylate. Techniques for minimizing odors should be considered for unloading, storage, sampling, and during laboratory work. Effective ways of minimizing odors during an accidental release should also be considered.

Final emission control devices include thermal oxidizers and liquid scrubber systems. An activated carbon bed is frequently used after a scrubber system.

Chemicals are frequently employed to absorb and react with the acrylate. The use of masking agents is not recommended. A typical commercial scrubbing solution is comprised of water, sodium hydroxide, a water-soluble amine, and a water-soluble alcohol. An example is 20% sodium hydroxide, 10% diethanolamine, 6% isopropyl alcohol, and balance water. With time, the sodium hydroxide causes saponification of the acrylate ester to sodium acrylate and the alcohol. The amine is an accelerator that quickly reacts as a Michael addition reagent. The isopropyl alcohol is a co-solvent that increases the solubility of the acrylate in the aqueous solution. A straight aqueous sodium hydroxide solution can also be used but more residence time and lower gas velocities may be necessary to achieve comparable results.

Activated carbon beds can be installed after a scrubber to help eliminate all odor. **HOWEVER, CAUTION: IF VENTS THAT COULD CONTAIN HIGH CONCENTRATIONS OF ACRYLATES GO DIRECTLY TO A CARBON BED THERE CAN BE A FIRE AS A RESULT OF THE HEAT OF ADSORPTION.** Aqueous amine solutions can be used to clean fittings, glassware, and equipment upon opening of closed systems. This includes truck fittings, dip pipes, flex hose fittings, sample devices, etc. Aqueous amine solution can also be used to help minimize odors during an accidental spill. The amine solution is sprayed onto the pool of acrylate by using a liquid applicator. Prepared solutions may be commercially available; your supplier may be able to provide a recommendation. The spill is then cleaned up by immobilizing with a suitable absorbent or with a vacuum truck, depending on the quantity involved. (Note that handling volatile organics under vacuum may reduce the flash point, increasing risk of fire or explosion.) The chemically treated acrylate spill can also be diluted with a large quantity of water and sent directly to a permitted biological treatment facility. Another approach for minimizing odors during a spill is to apply firefighting foam. The foam helps to blanket the acrylate and prevent the escape of vapor.

Dry break disconnects are frequently used on both liquid and vapor lines to minimize the release of acrylates when flexible transfer hoses are disconnected. The liquid transfer hoses are usually blown out with air or mix gas (5 to 21 Vol.-% of oxygen) before disconnecting. Some loading and unloading systems have a vacuum clean out system to minimize odors. Before disconnecting and opening the system, a vacuum is pulled to suck the liquid out and vaporize the remaining liquid film on the interior of the piping system. Closed sample systems can help to minimize odors. Spraying all sample bottles and equipment with an amine solution and wiping them down if a film of acrylate is suspected is recommended to reduce odors. All sample bottles and equipment brought into the laboratory should be completely odor-free. Performing all open transfers of acrylates in a vent hood avoids odors. It is important that contaminated sample bottles and glassware be thoroughly cleaned before being removed from the vent hood.

7.2 DESIGN CONSIDERATIONS

Some design considerations for bulk acrylate storage facilities and accessories are given in Sections 7.2.1 through 7.2.15. Table 7-1 summarizes the special recommended design features covered in these sections. The design of bulk storage facilities is typically accompanied by a risk analysis using methodologies like HAZOP, or similar. The ultimate goal is to reduce the risk associated with storing acrylates. Risks can be reduced through inherently safe design wherever possible. Additional protection can be achieved by detection and protection through electric and electronic devices meeting local codes.

Certain historical incidents with acrylates resulted in situations that caused major emissions and could have resulted in injuries and even fatalities. Root cause analysis suggested that the implementation of temperature recording(s) to detect an early temperature increase could have avoided the incident. Temperature monitoring might indicate a beginning polymerization reaction with the potential to result in subsequent rupture of a tank or a vessel and a potential Boiling Liquid Expanding Vapor Explosion (BLEVE).

It is recommended that fail-safe positioning of automated valves and emergency backup power for critical instrumentation be included in the design. Each facility is responsible for following all codes and regulations applicable to the geographic location of the facility. Design features of an acrylate storage facility are given as examples in Figures 7.1 and 7.2. A complete acrylate audit and assessment protocol for acrylate storage can be found in *Appendix F*. Contact your acrylate supplier for additional guidance.

7.2.1 Temperature Control of Bulk Storage Tanks and Accessories

The common practice is to maintain acrylate storage tanks and piping systems at ambient temperatures (no heating or cooling). However, in some storage systems the acrylate is cooled in order to lower the vapor pressure. Some of the potential advantages of a lower vapor pressure may include reduced flammability risk, fewer emissions, less risk of odor complaints, and reduced condensation/polymerization in vent lines.

Design of the entire storage and handling system to prevent accidental exposure to high temperature heat sources such as steam, pumps, solar heat and electrical devices reduces the risks of unintended polymerization. **EXPOSURE OF STORED ACRYLATES TO HIGH TEMPERATURE HEAT SOURCES CAN RESULT IN DANGEROUS POLYMERIZATION.**

Since critical conditions are typically detected by a temperature increase, it is suggested in this manual to have at least three subsequent temperature alarms implemented:

First alarm level: Supplier recommended storage temperatures are typically a maximum of 35-40°C. Consider setting the First alarm level at or slightly above typical storage conditions. For example, if the normal storage temperature is 30°C, consider an alarm at 32°C. Temperatures at or above this alarm level should be investigated immediately. For example, consider checking the functioning of the temperature sensors for plausibility, checking the temperature increase rate, and verifying the temperature increase by circulating the tanks contents which removes temperature layers. Once it is verified that the temperature increase was not caused by a malfunction or a localized temperature effect, initiating primary countermeasures can prevent unintended polymerization.

Second alarm level: This alarm is based on the assumption that the material may be polymerizing and triggers an emergency response scenario. Typically, the second alarm level is set at 40-50°C. Initiating secondary countermeasures as outlined in *Chapter 11* can halt polymerization.

Third alarm level: If all countermeasures to stop heat up of the tank contents are unsuccessful and the tank reaches this alarm level, then there is a possibility that the tank will rupture with a subsequent escape of an ignitable vapor cloud. Typically, the third alarm level is set at 60°C.

Small diameter piping systems located outdoors (including valves, pumps and filters) may experience solar heating if left liquid-full for prolonged periods of time in a static state. Potential polymer formation problems in such systems can be avoided by periodic circulation, blowing the system with a gas containing minimum 5 Vol.-% of oxygen, or by draining the system. It is also possible to reduce the risk of polymer formation problems related to solar heating by covering or insulating piping in order to prevent prolonged exposure to direct sunlight.

7.2.2 Recirculation and Storage Tank Filling

Bulk storage tanks typically have either a dip tube ending shortly above the tank bottom or a side entry nozzle near the bottom as a tank inlet.

Dip tubes are normally tack welded to the bottom to assure static grounding and have an anti-siphon hole near the top.

Side entry nozzles are located below the minimum liquid level of the tank in order to avoid splashing into the vapor phase and subsequent electrostatic discharges.

If side entry nozzles are equipped with an eductor for improved mixing, submerging the nozzle with sufficient liquid layer when in use avoids the possibility of forming a stable aerosol and subsequent ignition from static charge development. Acrylate mist caused by splashing and spraying can be ignited well below the flash point.

Recirculation is beneficial for mixing tank inventory, replenishing dissolved oxygen and homogeneous temperature distribution throughout the liquid phase. Thus, acrylate storage systems are generally designed to allow non-routine recirculation as needed. There is some risk that heat introduced by the pump during prolonged recirculation could overheat the acrylate, especially if the system is insulated. Employing appropriate engineering safeguards and operating procedures helps to prevent excessive temperatures during recirculation.

Maintaining the dissolved oxygen content of the inventory keeps the inhibitor working. Recirculation of the contents on a regular basis will keep adequate oxygen dissolved in the liquid as long as the gas atmosphere above the liquid level consists of a minimum of 5 Vol.-% of oxygen. Avoiding a shortcut between inlet and outlet of the recirculation, e.g. by locating the fill pipe across the tank from the outlet, is recommended to improve circulation. Submerged nozzles and pipes can plug if not frequently utilized. Level monitoring instrumentation is recommended to avoid spills when filling a storage tank. Maintaining a minimum void volume of about 10% of blanket gas containing oxygen above the liquid ensures adequate oxygenation. Ensuring the inlet nozzle or eductor is submerged in liquid avoids splashing and static charges from developing. It is recommended that the level monitoring instrumentation include device(s) which alarm if the tank is filled above or emptied below a safe level. Equipping the tank with high level switches which shut off the unloading pump can help avoid a potential spill. If a differential pressure level indicator (bubbler type) is installed, a gas containing a minimum of 5 Vol.-% of oxygen must be used. Dry, oil free air is recommended for this service.

7.2.3 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 acrylate pumps. **DEADHEADED PUMPS CAN QUICKLY OVERHEAT AND CAUSE A VIOLENT POLYMERIZATION.**

Some options to help protect pumps from overheating/deadheading are given below; the choice of method of deadhead protection may vary from case to case and is generally based on a safety analysis.

- 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). To ensure proper functioning, such a recirculation line is designed to never be blocked (e.g., with locked open valves if valves are needed) and is 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.

Two different types of sensors are recommended in order to provide redundant protection from pump overheating.

Other considerations associated with pumping acrylates are given below.

- Double mechanical seal (with 5 to 21 Vol.-% of oxygen, if gas buffered) and magnetic drive centrifugal pumps are commonly used for acrylates service. Using instrument interlocks in these pumps prevents dangerous overheating in case deadheading accidentally occurs.
- Flushing seals and bearings in contact with acrylates ensures adequate cooling and lubrication. High surface temperatures can cause polymer particles to form.
- Air driven diaphragm pumps are occasionally used for acrylate service. Diaphragm pumps usually stop pumping if deadheaded and may not require instrument interlocks to protect against overheating.
- Truck mounted pumps are not recommended for unloading acrylates, 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 7.2.8.

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

7.2.4 Detecting Unsafe Conditions inside Bulk Storage Vessels

Critical conditions are typically detected by a temperature increase. A minimum of two independent temperature probes is recommended for storage tanks (check tanks, weigh vessels, and charge vessels) equipped with high temperature alarms specified by a HAZOP study.

The temperature probes are normally located in the liquid phase near the bottom of the vessel (preferably 180 degrees apart on the circumference of the tank)(*see* Section 7.2.1) . Circulating the tank contents prevents temperature variations inside the tank (*see* Section 7.2.2). Recording and monitoring the temperature signal continuously allows for trend analysis.

AN INEXPLICABLE TEMPERATURE INCREASE COULD BE AN EARLY WARNING SIGN OF POTENTIALLY UNSAFE CONDITIONS AND EARLY DETECTION ALLOWS LEEWAY FOR CORRECTIVE ACTIONS.

START IMMEDIATELY TO INVESTIGATE AN INEXPLICABLE TEMPERATURE INCREASE! EARLY DETECTION OF A HIGH TEMPERATURE INSIDE AN ACRYLATES VESSEL CAN FACILITATE TIMELY EMERGENCY RESPONSE TO A DANGEROUS INADVERTENT POLYMERIZATION AND MAY HELP AVOID SERIOUS INJURY AND/OR LOSS OF PROPERTY.

Pressure relief cannot be achieved via a rupture disk in the event of a runaway polymerization. A weak seam roof design is recommended instead. In general, floating roofs are not recommended because they limit the amount of headspace for oxygen. In some cases, however, floating roofs have been designed to incorporate the requirement for adequate oxygen-containing headspace (*please refer to* Section 7.2.2).

7.2.5 Avoiding Polymer Formation in Vent Nozzles and Vent Lines

The polymerization of condensed acrylate monomer vapors in storage tank vent systems can result in dangerous conditions by plugging critical pressure and vacuum relief lines. Liquid acrylate monomer condensed from vapor does not contain MEHQ stabilizer and is prone to form polymer. It is recommended that all critical vent nozzles and lines be routinely inspected for polymer, promptly removing any polymer found . As practical, the use of sloped vent lines to drain condensed liquid back to a vessel containing stabilized acrylate monomer can prevent plugging. Installing drain valves at low points in the vent system where condensed acrylate monomer may accumulate can similarly prevent plugging. It is recommended that all drain valves be capped or plugged to minimize the risk of a release.

There are several optional engineering modifications that have proven successful in reducing condensation in vent nozzles and piping help to minimize the risk of polymer formation. One option is to insulate vent nozzles and lines to help keep the temperature above the dew point of the vapor. The use of properly designed tracing as well as insulation further minimizes the risk of rapid polymer formation by further increasing the temperature of metal surfaces in the vapor space above the dew point. Another proven modification is to sweep nozzles that are prone to plug with a small amount of dry, oil-free non-condensable gas that contains 5 to 21 Vol.-% of oxygen. The intent of using a non-condensable gas sweep is to lower the dew point of the vapor to a temperature lower than the solid surfaces in contact with the vapor. In case condensed liquid does form, avoiding low points in the vapor lines may prevent it from accumulating and forming polymer. If needed, contact your acrylate monomer supplier for further guidance on minimizing polymer formation in vent systems.

7.2.6 Heating of Liquid Acrylate Monomer

HEATING OF LIQUID ACRYLATE MONOMER IN UNLOADING AND STORAGE SYSTEMS IS NOT RECOMMENDED. ACRYLATES DO NOT FREEZE AT AMBIENT TEMPERATURES. IT MAY BE NECESSARY TO PRE-HEAT LIQUID ACRYLATE AS PART OF A CHEMICAL PROCESSING STEP. IF SO, CONDUCTING A THOROUGH SAFETY REVIEW HELPS ENSURE THAT AN UNCONTROLLED POLYMERIZATION DOES NOT OCCUR. **EXPOSURE OF ACRYLATE TO HIGH TEMPERATURE HEAT SOURCES AND/OR KEEPING ACRYLATE AT ELEVATED TEMPERATURES FOR PROLONGED PERIODS OF TIME CAN BE DANGEROUS.**

7.2.7 Indoor Acrylates Storage Facilities

Each facility is responsible for following all codes and regulations applicable to the geographic location of the facility. The special risks associated with indoor acrylate storage facilities are generally 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 are carefully considered.

The design of the indoor facility typically provides for an odor-free work environment. Ensuring indoor acrylate storage facilities are well ventilated helps prevent local accumulation of vapors, which can have potentially harmful effects on personnel. It is suggested that local exhaust systems be considered to supplement the general exhaust system and ensure adequate air change rates. It is recommended that all laboratories be provided with a sufficient number of properly designed exhaust hoods. Venting all indoor bulk storage tanks outside of the building also prevents odors and vapor buildup inside.

7.2.8 Engineering Features for Environmental Protection

Each facility is responsible for following all environmental regulations applicable to the geographic location of the facility.

Spill containment helps protect public waterways and ground water. Dikes around storage tanks are used to contain spills. Properly designed dikes and flooring constructed of concrete which can hold 110 % of the entire contents of the largest tank are suggested. 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. 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. It is good practice to have both a level switch and a continuous level measurement device installed. Implementing high level alarms and interlocks further improves safety. (*See Section 7.1*) Vapor return lines are suggested for bulk unloading facilities to reduce emissions (*see Sections 9.4.2 and 9.5.2*). 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 is one of the considerations in the selection of pumps.

7.2.9 Engineering Considerations for Fire Control

It is highly recommended that engineering safeguards be provided to reduce 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 Chapter 11 on emergency response*.

Water monitors are suggested to help control acrylate fires and to cool acrylate containing equipment during a fire. Isolation with dike walls can be used to protect acrylate tanks from pool fires caused by other chemicals.

All acrylates discussed in this manual, with the exception of 2-Ethylhexyl Acrylate, form readily ignitable vapours at ambient temperatures. The flash points and other flammability characteristics are listed in *Chapter 3* in the corresponding table. When oxygen is present above the limiting oxygen concentration (LOC), ignition may occur in the presence of ignition sources. Besides common sources of ignition, it is recommended to investigate potential spark discharge from static electricity or improperly grounded and bonded vessels.

Acrylates flowing through or being discharged from a pipeline may generate static electricity. Hence, during transfer from one container into another, electrical bonding and proper grounding prevent static discharges. Splashing into a tank can be avoided by the use of a dip tube. If mixing nozzles are used in storage tanks (*see Section 7.2.2*), keeping the nozzles always well below the liquid surface avoids spraying. All permanent storage tanks that contain acrylates with low flash points are subject to regulatory fire protection equipment requirements. Except for emergency relief valves, outlets to the atmosphere generally are protected with flame arrestors and detonation traps. (*see Section 6.3*)

Exhaust gases loaded with acrylates are best purified in a wet scrubber using ordinary caustic, aqueous organic amines or a mixture of both (*see Section 7.1.1*). For the final off gas purification, an activated carbon cartridge can be used. The heat of absorption for all acrylates on activated carbon is unusually high. Therefore, if highly loaded exhaust gases are passed over activated carbon, ignition of the carbon bed may occur. Active carbon cartridges are therefore not normally used for the removal of acrylates from exhaust gases, unless the gases are pre-treated in a wet scrubber. Separation of carbon cartridges from the tank by a flame arrestor helps prevent flame flashback into the tank .

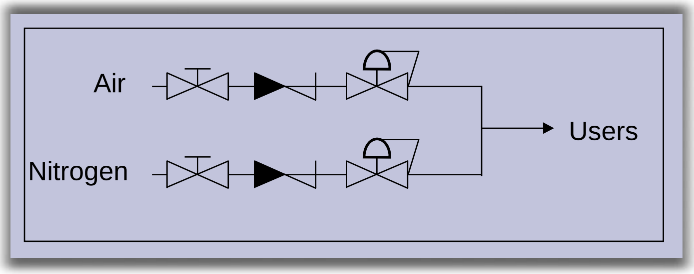
However, if a fire does occur in or close to a tank farm containing acrylates, cooling tanks and pipes by spraying with plenty of water can prevent acrylates from polymerising. A restabilization (shortstopping) system can be installed to allow the quick addition of a suitable anaerobic inhibitor such as phenothiazine (PTZ) in the event of a fire. Acrylates containing PTZ are much less likely to polymerize violently during a fire (*see Section 11.1.3*).

Small fires can be fought with carbon dioxide or dry chemical extinguishers. For larger fires, foam is suitable.

All esters are immiscible with water and lower in density than water. Consequently, water will not adequately extinguish a fire. A foam system with injection nozzles can be used to extinguish an acrylate fire (*see Section 11.3*).

7.2.9.1 Mixed Gas Systems (Lean Air Systems)

Standard industry handling practice for non-acrylate flammables is to use inert gas (nitrogen) for blowing of lines, pigging operations, and blanketing of tanks, but MEHQ requires the presence of dissolved oxygen for stabilization. To support inhibition, a minimum of 5 Vol.-% oxygen in the gaseous atmosphere is recommended. Methyl, Ethyl and i-Butyl Acrylates readily form, and Butyl Acrylate may form, flammable mixtures with air at ambient temperature. To address flammability concerns while maintaining the necessary oxygen for inhibition, a mixture of air and nitrogen may be employed. Oxygen concentration levels below the LOC (Limiting Oxygen Concentration) ensure that there is no flammable atmosphere in the tank vapor phase. The LOC of Methyl Acrylate, Ethyl Acrylate, i-Butyl Acrylate and Butyl Acrylate are approximately 8.5, 9 and 9.5 Vol.-% respectively. Lean air or mixed gas are terms used to define a gas with less than 21% oxygen, the oxygen content

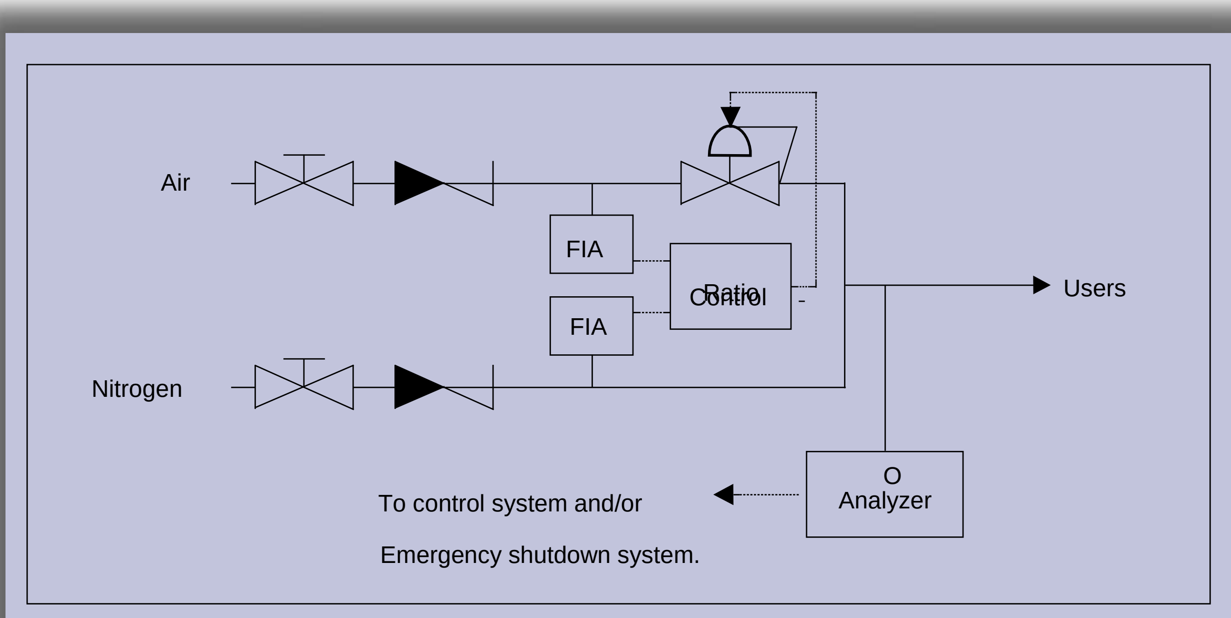


of atmospheric air. This would be a dry, oil and rust-free inert gas, such as nitrogen, that is mixed with air or oxygen to obtain oxygen levels between 5-21 Vol.-%. If the tank will be operated with oxygen content above the LOC, measures must be taken to prevent ignition of the flammable atmosphere. (see ***Section 7.1***)

An air-nitrogen mixing station can be designed to yield a gas containing 5 Vol.-% oxygen. Carefully considering equipment measurement tolerances helps ensure the operating range remains comfortably below the LOC and above the minimum recommended oxygen concentration (5 Vol.-%). For example, if analysis of the proposed mixing station design shows that the tolerance is +/- 1.5%, then the setpoint of the system would be 6.5 Vol.-% to ensure that the oxygen concentration is always above 5 Vol.-%. Reviewing the design of the mixing station with local safety personnel can ensure that it meets the criterion for both protection from flammability of the material and for protection from unexpected polymerization through all normal and emergency operations depending on the application and desired safeguards. An air-nitrogen mixing station can be designed as indicated below.

In some applications, for example where tank vents are collected into a header for incineration, there may be safety concerns that prevent the use of air to blanket flammable acrylates. Carrying out an appropriate safety analysis and consulting regulations for your area and application helps ensure the system is compliant and safe.

Never use an inert atmosphere when storing or handling Acrylates; make sure that oxygen is always > 5 Vol.-% in the gaseous atmosphere. (*See Section 6.1*)



FIA = Flow Indicator

7.2.10 *Engineering Controls for Contamination Protection*

Equipping the unloading pump with a clean dedicated unloading hose helps prevent contamination that can result in unintended polymerization.

Following best practices to prevent back-flow of liquids also avoids contamination; e.g., having check-valves in the filling line, or installing automated devices to prevent siphoning from other equipment back into the storage tank. Similarly. designing the venting system to avoid backflow of gases from other tanks vent is also recommended, e.g. using pressure control (PC) valves or dedicated vent lines. Avoiding by any means the accidental entry of incompatible substances into an acrylate storage tank either via liquid lines or via the vent system helps prevent contamination and unintended polymerization.

7.2.11 *Materials for Construction and Sealing in Acrylate Service*

Proper choice of materials of construction is important for safety, health, and protection of the environment. Some specific guidance for acrylate service is given below. Your supplier can provide further information.

Typical material of construction for tanks and pipes in general is carbon steel. Although carbon steel is acceptable for use with acrylates, the formation of rust may be a problem with product quality (color). Iron ions (Fe^{3+} have been shown to be a weak polymerization initiator. If carbon steel is to be used, special procedures should be used to prepare the tank for use. It is recommended to contact your supplier in such a case.

Phenolic-lined steel and stainless steel can also be used and may offer advantages in certain applications (*see* Section 8.3). Contact your supplier for a recommendation.

Preferred gaskets are made of PTFE, cross- linked EPDM, stainless steel with graphite coating or Kalrez® and specified according to the local emissions regulations.

Contact with copper or copper containing alloys is generally not recommended. Exposure to copper may result in adverse effects on the monomer properties.

7.2.12 *Venting of Bulk Storage Tanks*

Depending on the locations of the facility, various codes and regulations will be applicable. Each facility is responsible for following all applicable regulations.

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 7.2.5) and to ensure operability. The make-up gas supplied must contain 5 to 21 Vol.-% of oxygen. Dry, oil-free gas is preferred. The American Petroleum Institute (API) bulletin 2516 provides information related to the design and operation of conservation vents.

Typically, the maximum tank level allows for 10% void volume. This provides adequate oxygen-containing gas to keep the MEHQ inhibitor activated. Connecting the storage tank to an off-gas treatment system ensures proper venting. Off-gas treatment can either be done through scrubbers, incinerators, or thermal oxidation units. Local, state, and federal regulations may apply. Contact your supplier for additional guidance.

Please note: Avoiding the accidental entry of incompatible substances into an acrylate storage tank via the vent system helps prevents contamination and unintended polymerization.

For normal operations, a combination pressure-vacuum relief valve (PRV), sometimes referred to as conservation vent valve, is frequently employed to help minimize the multiplicity of equipment and nozzles. Note that a relief device to adequately relieve a runaway polymerization, would have to be too large to be practical. The size and output of the feed pumps are adapted to the venting capacity. It is recommended to have a separate PRV with a higher positive set point installed in addition to a standard PRV valve. Taking precautions to minimize condensation of acrylates in vent nozzles and lines helps ensure venting lines remain open. Acrylates condensed from vapor do not contain MEHQ stabilizer and are prone to form polymer. Polymer can plug critical pressure and vacuum relief lines. Sloped vent lines can drain condensed liquid back to a vessel and liquid drains can be considered where stagnant acrylates may occur. Polymer formation is likely in stagnant pockets.

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. Keeping these lines free of polymer and adjusting the vent conservation valves correctly helps contain acrylate vapors during unloading and loading.

The need to install flame arresters in vent lines may depend on the acrylate to be stored and the applicable regulations and codes of a given region, as well as the flash point of the acrylate and the flammability of the tank vapor phase. Routine inspections of the conservation vent system and the flame arrestors are recommended to ensure effective functioning and to remove any polymer. If a tank is equipped both a normal vent and an emergency venting device that is maintained in a closed position, a flame arrestor would not normally be installed on the emergency device.

7.2.13 Emergency Venting of Bulk Storage Tanks

Each facility is responsible for following all codes and regulations applicable to the geographic location in which it is located. Standard practice is to design storage tank emergency venting capacity for the vapor generation rate resulting from a pool fire around the tank.

THIS TYPE OF DEVICE WILL NOT PROVIDE ADEQUATE RELIEF IN THE EVENT OF AN UNCONTROLLED OR RUNAWAY POLYMERIZATION. *There is no known method for reliably relieving pressure from a run-away polymerization of acrylates in a tank.* Requirements for venting tanks containing flammable liquids can be found in OSHA standard 29 C.F.R. § 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. Inspecting emergency vent devices once a year to remove any polymer helps ensure operability. If the device is found to be fouled, increasing the inspection frequency ensures the device remains clean. Storage tanks installed indoors typically are designed to route the emergency vent to the outside. Contact your supplier for additional guidance.

It is recommended that weak seam roofs be used when possible in order to provide maximum venting in case of a violent polymerization.

7.2.14 Other Bulk Storage Tank Accessories

A 10% minimum void volume of blanket gas containing 5 to 21 Vol.-% oxygen should be maintained above the liquid.

Bulk storage tanks typically have either a top entry fill pipe or a side entry nozzle for unloading and circulating the acrylates. Top entry fill pipes are normally tack welded to the bottom to assure static grounding and have an anti-siphon 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. Submerging the nozzle tip when in use avoids 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. 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. Methyl, Ethyl and i-Butyl Acrylates readily form, and Butyl Acrylate may form, flammable mixtures with air at ambient temperatures. When flammable mixtures may be present, it is important that the liquid level be above the pump suction line before starting the pump. Many tanks are also equipped with a high-high level switch, which shuts off the unloading pump before a potential spill. A differential pressure level indicator (bubble type) is frequently used in acrylate service. A dry, oil-free gas containing 5 to 21 Vol.-% of oxygen must be used for bubble type level indicators with acrylates.

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

7.2.15 Summary of Special Recommended Design Features for Bulk Acrylates Storage Facilities and Accessories

Table 7-1 summarizes the special recommended design features for bulk acrylates storage facilities and accessories. The table also includes references to the related information given in Sections 7.2.1 through 7.2.5.

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

FEATURE	SECTION REFERENCE
Install flame blocking devices, such as flame arresters, as justified.	6.2
Install control devices as needed to provide an odor-free work environment.	7.1.1
Do not use high temperature heat sources such as steam or uncontrolled electric elements for direct heating of acrylates.	7.1, 7.2.1, 7.2.4
Install two independent temperature probes on all bulk acrylate 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 accidental overheating of acrylates by pumps.	7.1, 7.2.2
Take precautions to limit the temperatures of pump seals and bearings in contact with acrylates.	7.2.2
Provide the capability of non-routine circulation in bulk acrylate storage tanks as needed.	7.1, 7.2.1, 7.2.3
Provide gas containing 5 to 21 Vol.-% of oxygen (dry, oil-free gas is preferred) for blanketing acrylate storage vessels and for blowing out acrylate lines.	7.1, 7.2.4, 7.2.9, 7.2.10, 7.2.12
Take precautions to minimize potential condensation of acrylate in vent lines. This can cause polymer formation resulting in plugged pressure and/ or vacuum relief lines.	7.1, 7.2.4, 7.2.10, 7.11
Provide engineering safeguards to reduce the risk of a violent inadvertent polymerization inside an acrylate bulk storage tank during a fire.	7.1, 7.2.5, 7.2.7
Design bulk acrylate 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 acrylates, 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, 11-1, and 11-2

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

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

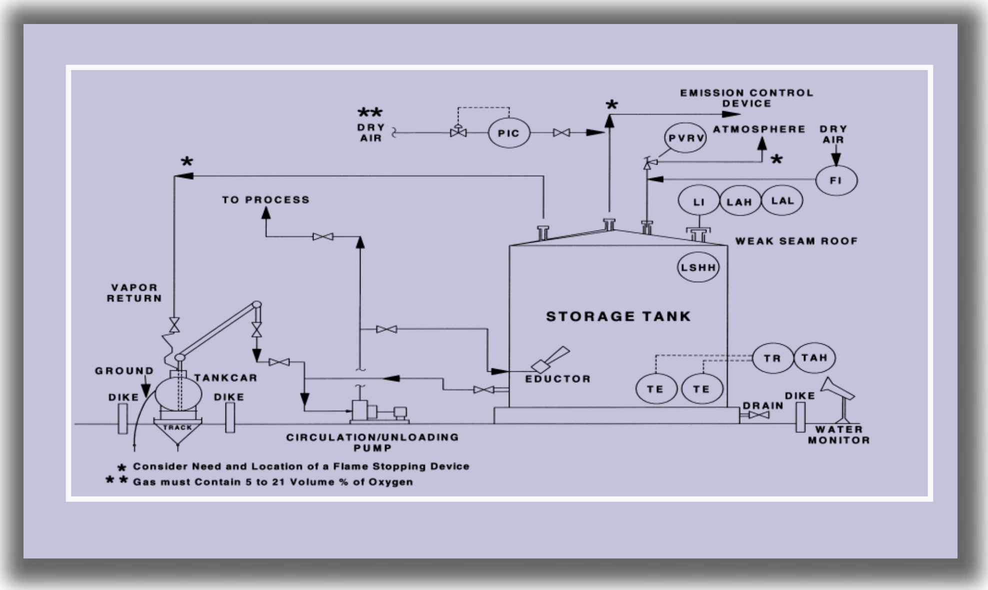
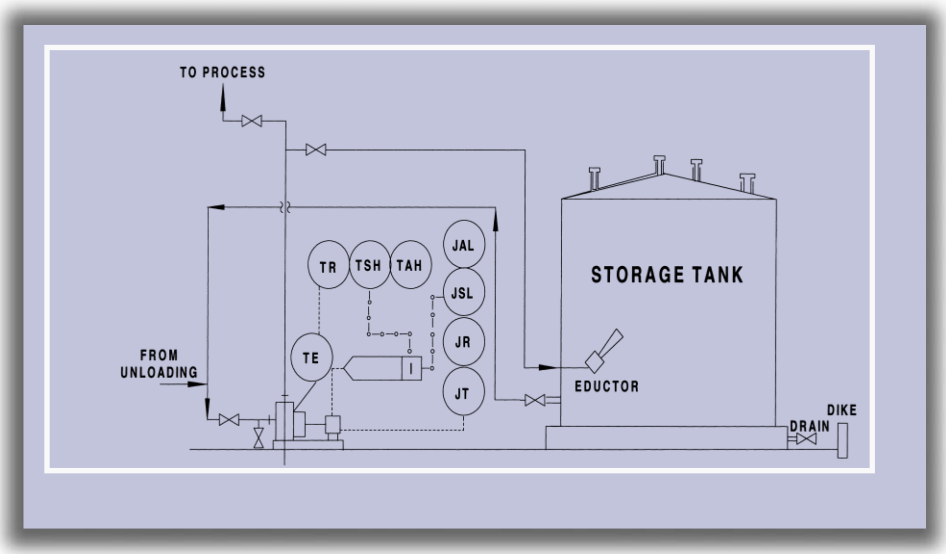


Figure 7-2: Example of an Acrylate Monomer Pump Loop

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



8.1 GENERAL CONSIDERATIONS

Because of the hazardous nature of equipment preparation and cleaning, typically a qualified multifunctional team plans each step of the job in detail and considers all possible hazards such as respiratory hazards, potential for personnel exposure, flammability, environmental releases, risk of polymerization and contamination. This team can write stepwise safe work procedures which clarify hazards, preventive measures and personal protective equipment to be worn at each step.

Performing equipment preparation and cleaning under the direction of trained personnel who are familiar with the written stepwise safe work procedures helps ensure the work proceeds safely. Having all involved personnel understand the potential hazards pertaining to the job and the importance of maintaining an odor-free work environment before work is initiated also helps maximize safety.

8.2 PREPARATION OF THE TANK AND EQUIPMENT

The tank or equipment to be cleaned is first be emptied of all liquids. Some liquid can remain with the equipment after it is emptied; generally, the residual monomer is removed, stabilized with PTZ or disposed of. The amount will vary from tank to tank depending on the geometry of the outlet nozzles and piping and the flatness of the tank floor. Pipe lines into or out of the tank are typically disconnected, preferably by removing a complete small section, provided there is a blank flange on the open end to protect against human error and unsuspected leaks. Valves and blind flanges in the pipe line alone are usually insufficient.

If pipe sections are to be removed and flanges opened, the lower bolts are loosened first. Wearing appropriate PPE can avoid personal contact with any liquid draining or dripping from the equipment. Any spillage from the lines or equipment can be contained, absorbed or removed immediately by flushing with water or otherwise in compliance with all local regulations and restrictions.

8.3 COMMISSIONING ACRYLATES BULK STORAGE FACILITIES

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

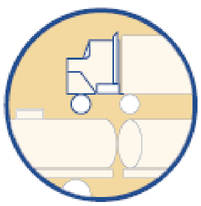
- Break all flanges at equipment; instruments, pump and exchangers are not flushed through.
- Water flush all lines then reassemble equipment.
- Fill tank with high-purity water, checking all possible instrumentation interlocks.
- Perform water run. Run as much of the system as possible to identify problems and tune control loops.
- Drain water from tank and blow/drain all lines.
- Rust can lead to local polymer formation and product discoloration, both of which may adversely affect end use applications. The interior of newly constructed steel tanks can be sand blasted to a white metal and vacuum cleaned to remove rust. If the rust-free steel tank is not soon filled with acrylate monomer, blanketing with dry air or dry mix gas containing 5 to 21 Vol.-% of oxygen retards rusting.
- The rust removal and rust prevention step is not necessary for stainless steel or coated tanks. Such tanks are typically dried and blanketed with a dry gas containing 5 to 21 Vol.-% of oxygen before receiving product.
- Do not use incompatible substances, such as nitric acid, for preparing acrylate systems. See *Section 6.1* on Polymerization and *Appendix A* for a list of Incompatible Materials. Contact your acrylate supplier if additional guidance is needed.

8.4 CLEANING ACRYLATE BULK STORAGE FACILITIES FOR DECOMMISSIONING

The following are the typical steps included in standard operating procedures for cleaning acrylate bulk storage facilities for decommissioning; contact your supplier for more information.

- Blow all product from lines and accessories back into tank using a gas with 5 to 21 Vol.-% of oxygen. Take precautions not to damage any sensitive equipment.
- Remove product from the tank.
- Flush all lines and accessories with water.
- One or all of the following may be needed to thoroughly remove odorous vapors:
- Open tank and use additional water wash if odor is found. Take precautions not to damage any sensitive equipment or seals.

- Steam all lines and accessories until clean. Take precautions not to damage any sensitive equipment or seals.
- Wash with 5 to 8 percent caustic to convert the acrylate into less odorous (alcohol and acrylate salt). Remove caustic solution and rinse thoroughly with water.
- Flush with air to an emission control device (*see* Section 7.1.1).
- Repeat the above steps as needed to remove odor.
- Wash the tank with 5 to 8 percent 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 can be entered if it is free of odor and tested for flammable vapors, oxygen content and residual caustic (if used). Follow all applicable regulations concerning vessel entry.
- Dispose of any residual product, polymer, cleaning solutions and rinse solutions at approved facilities.



9 SAFE TRANSPORT OF ACRYLATES

9.1 PERSONAL PROTECTIVE EQUIPMENT (PPE) FOR UNLOADING AND HANDLING

Full protective clothing for unloading and handling is typically used as follows: a chemical resistant splash suit, gloves, boots and eye protection. Regulatory industrial hygiene exposure limits should be considered when selecting proper respiratory protection. Clothing made of supported neoprene, neoprene, or other suitable material can protect the body against accidental acrylate splashes. Full eye protection including plastic shields with forehead protection in addition to chemical splash goggles can prevent accidental splashes from entering the eyes. NIOSH-approved respiratory protective equipment may be required in the US; each facility is responsible for following all applicable codes and regulations.

9.2 GENERAL CONSIDERATIONS

The following are general considerations that apply to all modes of transportation for acrylates. (*See also Chapter 6 for Instability and Reactivity Hazards).* A one-page safety guide summary for the transportation of acrylate can be found in *Appendix C*. Each transporting company is responsible for compliance with all applicable laws and regulations.

Methyl, Ethyl, i-Butyl and Butyl Acrylates are classified as "Flammable Liquids," as defined in DOT regulations 49 C.F.R. § 173.120(a). In the US, these acrylates are packed in DOT-compliant containers when shipped. The International Maritime Dangerous Goods Code (IMDG) classification for these acrylates is "Flammable." International shipping requirements differ depending on the countries involved and the shipping route and mode of transportation. 2-Ethylhexyl Acrylate is regulated as a combustible under DOT regulations. As a result, under 49 C.F.R. § 173.150(f)(2), this acrylate is packed in DOT-compliant containers when shipped in quantities greater than 119 gallons in the US. Similar restrictions may apply in other jurisdictions.

Transporting acrylates in an oxygen-containing (5-21 Vol.-%) atmosphere ensures the MEHQ inhibitor remains effective.

Using pure nitrogen or any other inert gas for unloading, sparging, blowing lines, or blanketing will reduce the amount of dissolved oxygen and is not recommended. The effectiveness of the inhibitor/stabilizer may be significantly reduced, resulting in a hazardous situation. Air or a gas mixture with 5 to 21 Vol.-% of oxygen are preferred for use in handling acrylates.

Contamination by incompatible materials (*See Appendix A*) may cause polymerization. Cleanliness and good housekeeping can prevent such contamination in containers.

Overheating of acrylates by adjacent cargo in multi-compartment vessels can result in unintended polymerization. maximum product temperature below the maximum recommended storage temperature of the acrylate prevents such.

Steam is not used to clean a tank with acrylic esters or to heat acrylic esters to avoid overheating.

Heating acrylates in any way for transportation or storage can result in unintended and hazardous polymerization. PRODUCT TEMPERATURES OF 40°C (104°F) OR HIGHER MAY INDICATE A HAZARDOUS SITUATION AND SHOULD BE IMMEDIATELY INVESTIGATED.

DOT regulations (49 C.F.R. § 173.24a(d)) require that drums are filled so that they will not be liquid full at 55 **°C** (131 °F). DOT regulations (49 C.F.R. § 173.24b(a)(1)) also require that bulk containers are loaded so that they have at least 1 percent void volume at 46°C (115°F) for uninsulated tanks and at 41°C (105°F) for insulated tanks. Regulations in other countries outside of the US may vary.

Samples have the same minimum void space requirements as drums. Retained samples can be stored for no more than a year in a cool dark place. Plastic coated amber glass bottles are recommended for handling and storing small amounts of acrylates.

The Non-Bulk Performance Oriented Packaging Standards, promulgated by DOT at 49 C.F.R. Subpart L, §§ 178.500-.523, require testing of non-bulk acrylates shipping containers for Hazard Class, Packing Group, and Subsidiary Hazard Class as shown in *Table 9-1*. Your sample container supplier can perform testing and contractually 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 steel can or polyethylene receptacle with screw cap and polyethylene insert with DOT approved outer packaging.

Greater than 1 Gallon

UN 1A1, steel drum or steel drum with phenolic internal coating

UN 1H1, self-supporting high- density polyethylene drum.

Reference 49 C.F.R. § 173.202 for requirements for non-bulk packaging.

Requirements outside of the US may vary; each transporting company is responsible for referencing and complying with applicable national and local requirements prior to shipping any acrylate substance.

9.2.1 Relevance of SAPT and Recently Finalized Transportation Requirements to the Transportation of the Basic Acrylate.

Recent amendments to United Nations model regulations on the transportation of dangerous goods ("TDG") define "polymerizing substances" and impose certain requirements on their transport and have resulted in changes to national regulations.

"Polymerizing materials" are defined in the US at 49 C.F.R. § 173.124(a)(4), as well as IMDG Code 2.4.2.5, in the context of a new Division 4.1 . This Division requires classification of materials as polymerizing substances, and the taking of certain safety measures, if the material's self-accelerating polymerization temperature ("SAPT") is below 75 °C (167 °F) and certain other criteria are met. Of importance for acrylates, the third criterion for inclusion in Division 4.1 indicates that when a material already meets the definition of a Class 1 through 8, including combustible liquids, then the material is not within Division 4.1 and is not subject to testing for SAPT. Ethyl Acrylate (UN1917), i-Butyl Acrylate

(UN2527), Butyl Acrylate (UN2348) and Methyl Acrylate (UN1919) are in Class 3 and therefore are not also classified as Division 4.1.

2-Ethylhexyl Acrylate, which is classified as a DOT Class 3 Combustible Liquid in containers greater than 119 gallons, is not classified under the UN TDG or IMDG regimes as classes 1 – 8. However, testing of 2-Ethylhexyl Acrylate has determined that the SAPT for product as offered for transport by BAMM members is greater than 75°C and as such 2-Ethylhexyl Acrylate in any package is not classified under Division 4.1.

DOT Special Provision 387 (49 C.F.R. § 172.102), IMDG Code SP 386, and equivalent regulations in other jurisdictions, separately regulate polymerizing materials designated as "stabilized." This includes acrylic acid and the four acrylates named above. In the HM-215N final rule adding this new provision, DOT stated "This special provision sets forth the transport conditions when stabilization, or prevention of polymerization, is provided through the use of a chemical inhibitor. When a substance is stabilized via use of a chemical inhibitor, it is important to ensure that the level of stabilization is sufficient to prevent the onset of a dangerous reaction under conditions normally incident to transportation." 82 Fed. Reg. 15,796, 15,813 (Mar. 30, 2017). DOT further stated "for materials specifically identified in the HMT (Hazardous Materials Table) by name (including n.o.s. entries) no additional testing is required to determine if the material is polymerizing." 82 Fed. Reg. at 15,818. These Special Provisions do not contain a direction to determine an SAPT for these materials.

Thus, the assignment of these Special Provisions means the material must be stable for the conditions and duration of transport. BAMM's member companies take measures, including chemical stabilization, to prevent polymerization events during transport and to comply with the regulations. Member companies have each developed data on the stability of these and other products under transportation conditions, and producers have a long history of safe transport of their products. Contact the shipper for further information.

Table 9.1: Summary of Shipping and Placarding Acrylates

Table 9-1: Summary of Shipping and Placarding Acrylates

Shipping Information	Methyl Acrylate	Ethyl Acrylate	n-Butyl Acrylate	2-Ethylhexyl Acrylate
DOT Classification	Flammable Liquid	Flammable Liquid	Flammable Liquid	Combustible Liquid
Shipping Name	Methyl Acrylate, stabilized	Ethyl Acrylate, stabilized	Butyl Acrylate, stabilized	Combustible Liquid, n.o.s. (2-Ethylhexyl Acrylate)
DOT Labels	Flammable Liquid	Flammable Liquid Corrosive	Flammable Liquid	None Required
DOT Placard	Flammable	Flammable	Flammable	Combustible
DOT I.D. Number	UN1919	UN1917	UN2348	NA1993 Bulk Only
Freight Class	Methyl Acrylate	Ethyl Acrylate	n-Butyl Acrylate	2-EthylhexylAcrylate
Hazard Class	3	3	3	Combustible Liquid
Packing Group	II	II	III	III
Subsidiary Hazard Class	–	8	–	–
DOT Emergency Response Guide No.	129P	129P	129P	128P

9.3 TRANSPORTATION INCIDENTS - IMMEDIATE ACTIONS

IN THE EVENT OF A SPILL, FIRE OR SUSPECTED POLYMERIZATION, IMMEDIATELY CALL CHEMTREC AT 1-800-424-9300 (or in Canada CANUTEC at 888-226-8832)**.** 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 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]) becomes damaged or a polymerization scenario is suspected such that delivery to destination cannot proceed safely, if it can be done safely without putting the driver or public at risk, it is recommended 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 are typically notified, and the public restricted from the area. **Immediately contact CHEMTREC at 800-424-9300** (or in Canada CANUTEC at 888-226-8832). CHEMTREC will contact the supplier. Further safety precautions are stipulated in the supplier's SDS for acrylates. *See Chapter 11 on Emergency Response for additional information.*

9.3.1 Bulk Cargo Temperatures

Heating acrylates in any way can result in dangerous conditions. Acrylates are shipped in bulk at ambient temperatures and do not need any special provisions for temperature control. Consequently, it is difficult to state any specific temperature range for normal acrylate cargo. An abnormally high temperature is an important indicator of a polymerizing cargo. **TEMPERATURES OF 40°C (104°F) OR HIGHER MAY INDICATE A HAZARDOUS SITUATION AND SHOULD BE IMMEDIATELY INVESTIGATED**. What is "abnormal" must be determined in the context of the cargo's history of ambient temperatures. For instance, a cargo temperature of 32°C (90°F) during cold winter weather is cause for serious concern and investigation. The same temperature during hot summer weather may be quite normal. Temperatures reaching 45°C (113°F) are generally cause for serious concern and immediate CHEMTREC notification regardless of ambient conditions. A 5°C (10°F) increase in temperature compared to the loading temperature is typically also a cause for serious concern and immediate CHEMTREC notification. **IF AT ANY TIME THE TEMPERATURE OF THE ACRYLATE REACHES 45°C (113°F) OR ABOVE OR HAS A TEMPERATURE RISE INCONSISTENT WITH THE EXPECTED IMPACT OF AMBIENT CONDITIONS, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300** (or in Canada CANUTEC at 888-226-8832)**.** CHEMTREC will contact the supplier. High temperatures can be a warning sign or indicator of a possible inadvertent polymerization. High temperatures can also *cause* an inadvertent polymerization and must be taken seriously. Isolating the bulk container as dictated by the circumstances and conditions at the time can help prevent overheating and unintended polymerization. *Also see Chapter 6 on instability and reactivity hazards and Chapter 11 on emergency response for more details*.

9.4 TRUCKS

The use of tank trucks for bulk transport of acrylates is authorized by DOT. Authorized bulk containers are described in DOT regulations 49 C.F.R. § 173.242. Refer to this regulation for complete bulk packaging information, including special requirements.

DOT approved containers include the following:

Tank Truck

Stainless steel or aluminum coiled and insulated with DOT specification MC-304, MC-307, MC-310, MC-311, MC-312, MC-330, MC-331, DOT-406, DOT-407 or DOT-412.

DOT Hazardous Materials Regulations are contained in 49 C.F.R. parts 100-180. It is recommended to consult these and/or other relevant national and local regulations for complete, up to date, tank truck specification packaging and placarding requirements. See *Table 9-1* for a summary of shipping and placarding information.

9.4.1 Carrier information

The shipper is responsible for providing tank trucks that meet all guidelines and regulations for transport of acrylates, inhibition of the product, and proper product temperature for shipping. These products may be temperature sensitive and flammable, and keeping the temperature of the empty vessel low enough ensures that the temperature of the loaded vessel is not negatively impacted. Drivers typically are thoroughly trained about the hazards of acrylic esters, and may be required to be trained by relevant regulations. Temperature measurement of the product in transit is not mandated and is rarely done. However, **SHOULD AN INCIDENT OCCUR, SUCH AS AN ACCIDENT INVOLVING THE**

TANK TRUCK, AN ELEVATION IN TEMPERATURE OF THE TANK TRUCK CONTENTS, THE PRESENCE OF A STRONG ODOR, OR ANY SUSPICION THAT THE ACRYLATE IN THE TRUCK IS POLYMERIZING, IMMEDIATELY CONTACT CHEMTREC AT 1-800-424-9300 (or in Canada CANUTEC at 888-226-8832)**.** CHEMTREC will contact the supplier.

Temperatures above the maximum recommended storage temperature as stated on the supplier's SDS (typically 35-40°C) may be a warning sign of a possible inadvertent polymerization and investigation may be warranted. If the high temperature is confirmed, e.g., via a second temperature measurement, preferably a dip probe, immediately contact CHEMTREC or the supplier.

9.4.1.1 Storage of Tank Trucks or Iso-Tanks

Tank trucks and Iso-tanks are discussed in this manual as transport vessels only. If these vessels are used for storage, it is recommended to contact the monomer supplier for guidance and precautions on storage conditions.

9.4.2 Unloading

The following procedures are suggested to reduce quality and safety risks during the unloading of acrylates. The contents of the truck generally are *positively identified* before they are transferred. If sampling is required, refer to site-specific procedures. Continuous monitoring of the unloading process is appropriate; refer to DOT requirements (49 C.F.R. § 177.834) or equivalent applicable regulations on the unloading of hazardous materials.

An emergency shower and eye wash station generally are directly accessible from and within 25 ft. (8 meters) of the unloading spot, and other sources of water are available for wash downs. Testing the emergency shower and eye wash station periodically helps ensure that they function properly. Personal protective equipment is usually worn while sampling or making any connections. Refer to OSHA or equivalent applicable regulations to determine the requirements relating to emergency showers, eye wash stations and personal protective equipment.

The use of proper equipment helps protect workers against spills. It is preferable that truck unloading facilities be level, paved and be located so that the truck can be easily and safely maneuvered. Providing a truck pad suitable to collect spillages can assist with appropriate disposal. Where access to the top of the container is needed, equipping the site with stairs and a platform ensures safety. An electrical grounding cable is required by DOT regulation, 49 C.F.R. § 177.837(b)-(c), and may be required under equivalent local regulations outside the US. Such a cable must be attached to the transport vessel while loading or unloading the container.

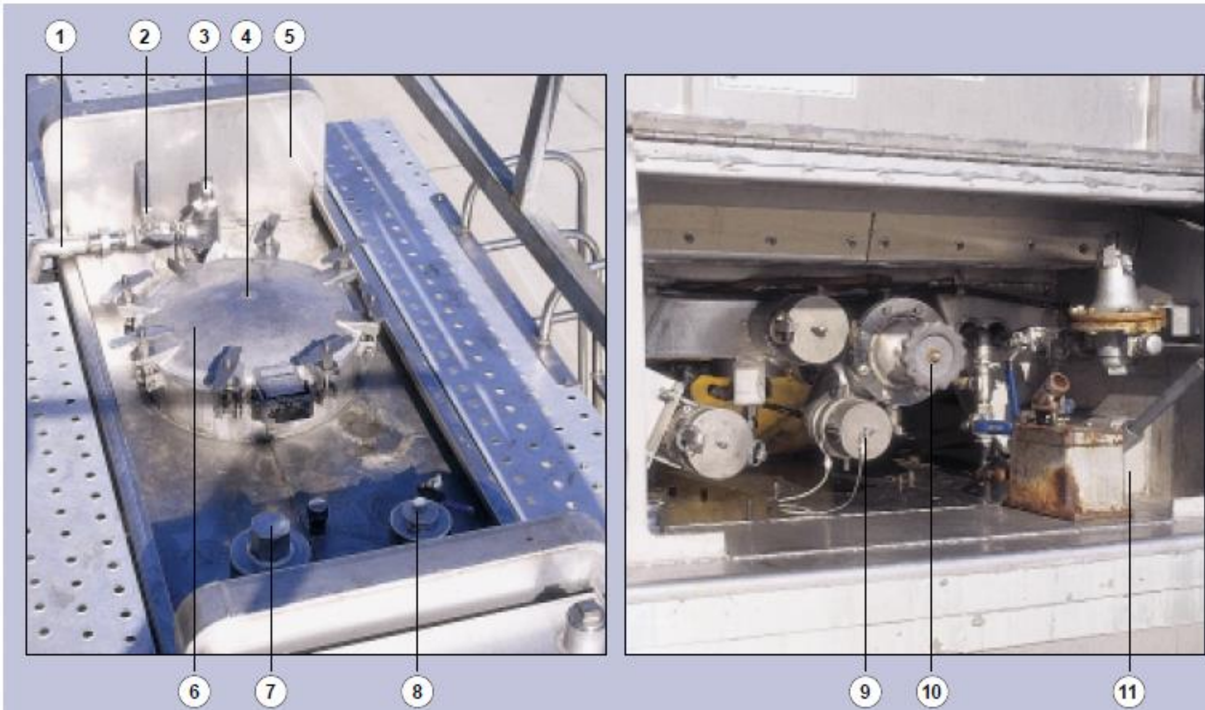
Having the piping for unloading on continuous circulation or arranged so the acrylates will drain toward the storage tank when transfer is stopped helps avoid clogging of piping or backflow. Where necessary, providing a check-valve on the unloading hose ensures that total tank contents will not spill in the event of a hose break. Measures to prevent backflow into the tank truck in the event the pump stops are also generally in place. Providing pump glands, flanged fittings and valve stems with splash collars in cases where personnel could be exposed to major acrylate leaks or sprays helps avoid such exposure.

Using dedicated hoses at the unloading site helps avoid contamination. These hoses usually are better maintained and thereby also minimize the risk of spills. Dry disconnect couplings are recommended to be provided on the unloading hose to reduce spillage during coupling and uncoupling operations. Alternatives to this procedure include flushing out hoses and lines with water or blowing them empty by lean air. Unloading acrylates using a vapor return line limits emissions to the environment. The vapor return line is recommended to be a standard connector.9.4.2.1 Unloading Trucks and Iso-tanks with Vapor Balancing System

The following recommended method for unloading a tank truck is by pumping with a vapor balancing system in which the displaced vapors are returned to the tank truck, or by 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. It is also recommended to refer to DOT or equivalent local regulatory requirements for unloading, as some of these steps may be mandated by regulation.

1. Spot the trailer and set wheel chocks. Stop the engine and apply the emergency brakes during unloading
2. Positively identify Acrylic Esters. Before unloading, inspect the vessel to ensure that it is not damaged or leaking. Compare the labels and the vessel identification number to ensure that they are identical to the transport documents
3. Connect tank truck grounding.
4. Check that the temperature of the cargo is consistent with previous receipts considering season of the year and is not higher than 45°C (113°F) before unloading. Normal temperature is near ambient temperature.
5. Verify that the receiving vessel will hold the entire contents of the tank truck.
6. Connect vapor hose and vent valve(s) to equalize pressure and confirm that all vapor valves and lines are clear. A plugged vapor line may result in pulling a vacuum on the truck as it empties. Negative pressure or vacuum conditions could cause the truck to implode.
7. Connect liquid line and open external (secondary) valve.
8. Open internal valve by using hydraulic pump and handle.
9. Start pump. Once flow has started, continue to monitor tank truck vapor return line and gauge to confirm flow.
10. When the trailer is empty, shut off pump and close both internal and external liquid discharge valves.
11. De-pressure liquid line, drain and disconnect hose, and replace cap. Place secondary containment under valve to capture any small spillage during disconnection.
12. Block in vapor system valves at 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 or equivalent regulatory 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: Acrylates Tank Trucks



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

9.4.2.2 Unloading Trucks with Pressure

An alternate method for unloading is to pressure out the acrylate by using a gas containing 5 to 21 Vol.-% of oxygen. The inhibitor, MEHQ, requires oxygen to prevent polymerization. DOT regulations restrict the use of air pressure with flammables, pursuant to49 C.F.R. § 173.24b(c). Similar requirements may apply in other jurisdictions. The pressure of the unloading gas is normally below 80 percent of the safety valve setting of the tank truck. The tank, vent system and procedure are also typically designed to manage the gas flow entering the tank once the truck has been emptied. The following are typical steps followed when unloading trucks with pressure:

1. Spot trailer and set wheel chocks. Stop the engine and apply the emergency breaks during unloading.
2. Connect tank truck grounding.
3. Positively identify acrylic esters. Before unloading, inspect the vessel to ensure that it is not damaged or leaking. Compare the labels and the vessel identification number to ensure that they are identical to the transport documents.
4. Verify that the receiving vessel will hold the entire contents of the tank truck. Check that the temperature of the cargo is consistent with previous receipts considering season of the year

and is not higher than 45°C (113°F) before unloading. Normal temperature is generally near ambient temperature.

5. Connect pressure supply hose and open vapor valve (s).
6. Open pressure supply hose valve enough to keep a positive pressure on the tank truck and confirm that all vent valves and lines are clear.
7. Regulate the unloading gas pressure so that it does not exceed 80 percent of the safety valve set pressure of the tank truck.
8. Connect liquid line and open external (secondary) valve.
9. Open internal valve by using hydraulic pump and handle.
10. When the trailer is empty, quickly block in all valves to avoid overwhelming the tank's vent system.
11. De-pressure liquid 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.

9.5 RAIL CARS

The use of rail cars for bulk transport of acrylates is authorized by DOT in the US. Authorized bulk containers are described in DOT regulations 49 C.F.R. §§ 173.241, 242 and 243. Refer to these sections for complete bulk packaging information, including special requirements.

DOT approved containers include the following:

Rail Car: DOT Class 103, 104, 105,109, 111, 112, 114, 115, 117 or 120. Such train cars are made as follows: Steel or stainless steel with stainless steel interior, unlined; Aluminum, non-flammable with aluminum interior, unlined; Aluminum, flammable with aluminum interior, unlined. See *Table 9-1* for a summary of shipping and placarding information.

Rail cars will typically have an eductor pipe and may have a gauging device and thermowell. Please consult the DOT Hazardous Materials Regulations (49 C.F.R. Parts 171-177) and/or other applicable national or local regulations for complete up to date rail car specification, packaging, and placarding requirements.

9.5.1 Carrier Information

The shipper is responsible for providing rail cars that meet all guidelines for transport of acrylates, inhibition of the product, and proper product temperature for shipping. Temperature measurement of the product in transit via rail is not mandated and is rarely done. However, **SHOULD AN INCIDENT OCCUR, SUCH AS AN ACCIDENT INVOLVING THE CAR, AN ELEVATION IN TEMPERATURE OF THE RAIL CAR CONTENTS, THE PRESENCE OF A STRONG ODOR, OR ANY SUSPICION THAT THE ACRYLATE IN THE CAR IS POLYMERIZING, IMMEDIATELY CONTACT CHEMTREC AT 1-800-424-9300** (or in Canada CANUTEC at 888-226-8832)**.** 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 or increasing temperatures and venting can be a warning sign or indicator of a possible inadvertent polymerization and investigation is warranted. Isolating of the car may be warranted, as dictated by the circumstances and conditions at the time. Also see *Chapter 6* on instability and reactivity hazards and *Chapter 11* on emergency response for more details.

9.5.1.2 Storage of Rail Cars

Rail cars are discussed in this manual as transport vessels only. If these vessels are used for storage, it is recommended to contact the monomer supplier for guidance and precautions on storage conditions.

9.5.2 Unloading

The following procedures are suggested to reduce quality and safety risks during the unloading of acrylates. It is recommended to positively identify the contents of the tank car before they are transferred. If sampling is required, refer to site-specific procedures. Continuous monitoring during unloading is appropriate; refer to DOT requirements (49 C.F.R. § 177.834), or equivalent national or local regulations, for monitoring unloading of hazardous materials.

An emergency shower and eye wash station are normally directly accessible and within 25 ft. (8 meters) of the unloading spot, and other sources of water is available for wash downs. Testing the emergency shower and eye wash periodically helps ensure that they function properly. Personal protective equipment is generally worn while sampling or making any connections. Refer to OSHA or equivalent applicable regulations to determine the requirements relating to emergency showers and eye wash stations and personal protective equipment.

The use of proper equipment helps protect workers against spills. An electrical grounding cable is required by DOT regulation, 49 C.F.R. § 177.837(b)-(c), and may be required under equivalent local regulations outside the US. Such a cable must be attached to the transport vessel while loading or unloading the container. Having the piping for unloading on continuous circulation or arranged so the acrylates will drain toward the storage tank when transfer is stopped helps avoid clogging of piping or backflow. Where necessary, providing a check-valve on the unloading hose ensures that total tank contents will not spill in the event of a hose break. Measures to prevent backflow into the rail car in the event the pump stops are also generally in place. Providing pump glands, flanged fittings and valve stems with splash collars in cases where personnel could be exposed to major acrylate leaks or sprays helps avoid such exposure.

Using dedicated hoses at the unloading site helps avoid contamination. These hoses usually are better maintained and thereby minimize also the risk of spills. Dry disconnect couplings are recommended to be provided on the unloading hose to reduce spillage during coupling and uncoupling operations. Alternatives to this procedure include flushing out hoses and lines with water or blowing them empty by lean air. Unloading acrylates using a vapor return line limits emissions to the environment. The vapor return line is recommended to be a standard connector.

9.5.2.1 Unloading Rail Cars with Vapor Balancing System

The following recommended method for unloading a tank car is by pumping with a vapor balancing system in which the displaced 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 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. It is also recommended to refer to DOT and equivalent regulatory requirements for unloading.

1. Connect the ground cable to the tank car.
2. Positively identify Acrylic Esters. Before unloading, inspect the vessel to ensure that it is not damaged or leaking. Compare the labels and the vessel identification number to ensure that they are identical to the transport documents.
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 cargo is consistent with previous receipts considering season of the year and is not higher than 45°C (113°F) before unloading. Normal temperature is generally near ambient temperature.
5. Examine all valves to be certain that they are closed before removing caps, plugs, or flanges.

6. Connect vapor hose to vent valve on tank car and open valves to equalize pressure and confirm all vapor valves and lines are clear.
7. Connect unloading line to the eduction valve, or if unloading from the bottom, the bottom outlet valve.
8. Close all bleeds on the unloading line and open the eduction valve, or if bottom unloading, open the bottom outlet secondary valve, then open the bottom outlet valve.
9. Start pump. Once flow has started, continue to monitor tank car vapor return line and gauge to confirm flow to avoid imploding the tank car.
10. When the tank car is empty, shut off pump and close all liquid discharge valves.
11. Depressure unloading line, drain and disconnect the hose and fittings.
12. Block in vapor system valve and vent valve on the tank car. Depressure and disconnect hose.
13. Re-install all flanges and plugs removed. Close and secure all housings. Follow DOT guidelines for securing rail car before shipment.
14. Per DOT regulations at the time of this publication, placards are NOT to be reversed.
15. Disconnect electrical ground and remove wheel chocks. Remove "tank car connected" sign, remove derailers, and unlock switches.

9.5.2.2 Unloading Rail Cars with Pressure

An alternate method for unloading is to pressure out the acrylate by using a gas containing 5 to 21 Vol.-% of oxygen. The inhibitor, MEHQ, requires oxygen to prevent polymerization. DOT regulations restrict the use of air pressure with flammables, pursuant to49 CFR 172.24b(c). Similar requirements may apply in other jurisdictions. The pressure of the unloading gas is normally below 80 percent of the safety valve setting. The tank, vent system and procedure are also typically designed to manage the gas flow entering the tank once the rail car has been emptied. This recommended 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. The following are the typical steps followed when unloading rail cars with 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. Positively identify Acrylic Esters. Before unloading, inspect the vessel to ensure that it is not damaged or leaking. Compare the labels and the vessel identification number to ensure that they are identical to the transport documents.
4. Verify that the receiving vessel will hold the entire contents of the rail car.
5. 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 cargo is consistent with previous receipts considering season of the year and is not higher than 45°C (113°F) before unloading. Normal temperature is generally near ambient temperature.
6. Examine all valves to be certain that they are closed before removing caps, plugs, or flanges.
7. Connect pressure supply hose to the vent valve on the tank car and open the vent valve.
8. Connect unloading line to the eduction valve, or if bottom unloading, connect to the bottom outlet.
9. Close all bleed valves on the unloading line, and open tank car valve or valves connected to the unloading line.
10. 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 percent of the safety valve set pressure stenciled on the side of the tank car.
11. Open unloading line valve.

12. When the tank car is empty, block in pressure supply hose valve, tank car unloading valve, and unloading line valve. This needs to be done quickly to avoid overwhelming the tank's vent system.
13. Depressure unloading line, disconnect and remove the unloading line and fittings from the tank car.
14. Vent the tank car down to minimal pressure before returning it to the shipper. If tank car cannot be depressured, add a tag stating, "tank car under pressure".
15. Block in vent valve on tank car. Depressure and disconnect pressure supply hose from the car.
16. Re-install all flanges and plugs removed. Close and secure all housings. Follow DOT guidelines for securing rail car before shipment.
17. Per DOT regulations at the time of this publication, placards are NOT to be reversed.
18. Disconnect ground and remove wheel chocks. Remove "tank car connected" sign, remove derails and unlock switches.

9.6 DRUMS AND INTERMEDIATE BULK CONTAINERS (TOTES)

The use of drums or IBCs (totes) for transport of acrylates is authorized by DOT. Non-bulk performance-oriented packaging standards in DOT 49 C.F.R. §§ 178.500-.523 require testing of non-bulk acrylates shipping containers for Hazard Class, Packing Group, and subsidiary Hazard Class as shown in Table 9-1. Your container supplier can perform testing and guarantee conformance to DOT requirements. The use of electrostatically safe drums and IBCs for loading and unloading is required for substances with a flash point below 60 ^{o}C (Volume II, Sec. 4.1.2 of the ``Orange Book'').

Containers that may test acceptably to DOT requirements for acrylates include the following. Requirements outside of the US may vary; it is recommended to reference local requirements prior to shipping any acrylate substance.

- 55-Gallon
  - UN 1A1, steel drum or steel drum with phenolic internal coating
  - UN 1H1, self-supporting high-density polyethylene drum.

Authorized bulk containers are described in DOT regulations 49 C.F.R. § 173.242. Refer to this section for complete, up to date bulk packaging information, including special requirements. DOT approved containers include the following:

- IBC
  - UN31A, 31B, 31Nor31HAl

Please consult DOT Hazardous Materials Regulations as contained in 49 C.F.R. parts 171-180 and/or relevant national and local regulations for complete, up to date specifications on packaging and placarding/labeling requirements. Even though there is a range of allowable options in IBC selection, the following factors are important in drum and IBC selection: flammability, permeability of the packaging material to Acrylic Esters, UV exposure, temperature exposure, mechanical strength vs. temperature, impact resistance, proximity of use to other containers containing materials of different flash points, and odor control. There is a variety of ways to manage these factors by container selection and by organizational means.

DOT, OSHA and potentially other regulations dictate properly labeling of containers of acrylates. Before transporting, storing or handling acrylates, obtaining, reading and understanding the current product and labeling information and the SDS (available from your supplier) can assist with compliance. Appropriate wording can be used on the label in addition to specific wording required by law. OSHA's Hazard Communication Standard, which includes labeling requirements can be found at 29 C.F.R. § 1910.1200. DOT's Hazardous Materials Regulation section on labeling can be found at 29 C.F.R. Subpart E.

Typically, regulations require placing the identifying label on each package and stenciling the generic name on the package. Proper DOT shipping information is summarized in Table 9-1. *Prevention of contamination can be difficult with IBCs (totes). If mishandled, the potential consequences for IBCs (totes) containing acrylates can be significantly worse than drums because of their increased size. For these reasons, it is strongly recommended to take extra care in the proper handling and transportation of IBCs (totes) containing acrylates.*

9.6.1 Carrier Information

Sources of heat, sparks, or flame are typically avoided to prevent heating and unintended polymerization of the acrylates. Shipment at ambient conditions is acceptable. It is not recommended to load or transport bulging or distorted drums. Bulging drums may indicate polymerization**. IF POLYMERIZATION IS SUSPECTED, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300** (or in Canada CANUTEC at 888-226-8832). CHEMTREC will contact the supplier and facilitate the establishment of communications between the personnel at the site and the supplier's emergency response team. *See also Chapter 6, Instability and Reactivity Hazards and Chapter 11, Emergency Response for more details.*

9.6.2 Storage of Drums and Intermediate Bulk Containers (Totes)

Acrylates are normally inhibited with 10 to 20 ppm of MEHQ to prevent polymerization.

The three most important considerations in shipping, storing and handling acrylates are to AVOID EXPOSURE TO ELEVATED TEMPERATURES, AVOID CONTAMINATION AND USE AN OXYGEN CONTAINING BLANKET GAS. To avoid unintended polymerization, consider the following:

- Not storing acrylate containers in direct sunlight.
- Contamination can cause an uncontrolled polymerization which may result in violent rupture of the container, fire, serious damage to the surroundings and significant environmental impact.
- The presence of oxygen is required for the inhibitor (MEHQ) to be effective. Lack of oxygen can cause an uncontrolled polymerization.
- Reusing drums or IBCs (totes) only if thoroughly cleaned or in dedicated service.
- Inspecting drums or IBCs (totes) periodically and following your supplier's shelf life recommendations (typically 1 year).

9.6.3 Handling Procedures

Methyl, Ethyl, i-Butyl and Butyl Acrylates are flammable liquids and should be handled accordingly pursuant to applicable regulations. Positively identifying the contents of the drums and IBCs (totes) before they are transferred helps ensure proper procedure is followed. The procedures outlined below are suggested to reduce risks during the handling of acrylates.9.6.3.1 Receipt of Drums and Intermediate Bulk Containers (Totes)

Acrylates are shipped in steel drums and stainless steel or high density polyethylene IBCs (totes). When a carload or truckload of drums or IBCs (totes) is received, leaving the doors of the car or truck open improves ventilation before entering. A persistent strong odor may indicate a leaky container.9.6.3.2 Emptying of Drums and Intermediate Bulk Containers

Acrylates mostly are flammable liquids and should be handled accordingly pursuant to applicable regulations. Positively identifying the contents of the drums and IBCs before they are transferred and used helps ensure proper procedure is followed. The following steps outline suggested procedures for safely emptying drums and IBCs:

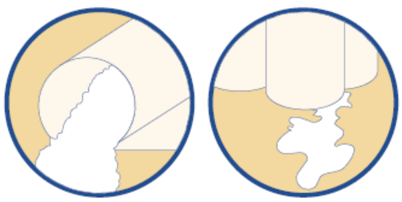
Drums and IBCs must be electrically grounded before starting and during the entire operation under DOT, OSHA and similar regulations and codes; similar requirements may apply in other jurisdictions. OSHA regulates bonding and grounding at 29 C.F.R. § 1910.106(e)(6); DOT regulates bonding and grounding at 49 C.F.R. § 177.837(b). A static-free dip pipe or flexible stainless steel hose is typically used to drain the Acrylate. If not designed to be electrostatically dissipative, composite plastic drums or IBCs are grounded, e.g., by placing into grounded housing, prior to starting the decanting operation.

To prevent ignition of the acrylate, avoid striking drums/IBCs and fittings with tools or other objects which may cause sparks or puncture.

Before removing plugs from acrylate drums or IBCs, it is recommended to locate the nearest emergency safety shower and eye wash station and put on all required personal protective equipment.

The preferred safe method for emptying drums and IBCs is by pumping. If drums or IBCs are emptied by gravity, the valves are normally self-closing. It is not recommended to use pressure to displace drums or IBCs' contents.

Providing adequate vacuum breaking prevents collapse of the drums or IBCs during emptying.



10 ENVIRONMENTAL CONSIDERATIONS FOR ACRYLATES

10.1 ENVIRONMENTAL FATE

Available studies indicate acrylates are unlikely to persist in the environment. Acrylates have medium to high mobility for adsorption and desorption to soils. They are not expected to bind to soil or sediment. If released to air, they will undergo photo-degradation within days. In contact with water, abiotic hydrolysis occurs very slowly. In water, sewage treatment plants, and soil, degradation is expected due to the action of bacteria in these media. Based on their physicochemical properties and biodegradability, there is no indication that acrylates have the potential to bioaccumulate.

10.1.1 Ecotoxicity

Ecotoxicity studies suggest that acrylates have a moderate to low acute toxicity in fish, algae, and daphnia. The moderate to low acute toxicity values (EC_{50} or LC_{50}) for the acrylate esters range between 1 and 100 mg/L. Chronic toxicity has been assessed using invertebrate studies conducted with ethyl and butyl acrylate. The 21-day chronic life-cycle studies with *daphnia magna* for acrylic acid show NOECS in the range of 1-10 mg/L, while NOECS for ethyl and butyl acrylate are in the range of 0.1-1 mg/L. In addition, several algal studies are available with NOECS in the same range. These values in combination with the ready biodegradability indicate moderate to low chronic toxicity.

10.2 DISCHARGES

10.2.1 General Information

A variety of national, federal, state and local regulations govern the release of any material to land, air or surface waters. Applicable regulations determine the appropriate response to any release or discharge of acrylates, including potentially appropriate response actions and reporting requirements. BAMM and its member companies believe the information below is factual; however, safe handling and compliance with national, federal, state and local laws and regulations is the responsibility of the company handling acrylates.

In the United States, a law called Resource Conservation and Recovery Act (RCRA) and regulations promulgated thereunder regulates the disposal or discarding of waste, including any volume of acrylates or material contaminated with acrylates. Based on RCRA hazardous waste criteria, found in 40 C.F.R. Part 261 Subpart C, acrylates or materials contaminated with acrylates may be considered a "Hazardous Waste" upon disposal and must follow certain storage, handling and disposal restrictions as outlined in RCRA. Ethyl acrylate is a listed waste (U113) per 40 C.F.R. § 261.33 and is therefore considered a hazardous waste in the US. Similar regulations may apply in other jurisdictions. 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 C.F.R. parts 260-266 and 268 (the RCRA regulations). [For additional information, see http://www.epa.gov/epawaste/hazard/index.htm]

Many industries are subject to the Toxic Release Inventory (TRI) requirements under § 313 of EPA's Emergency Planning and Community Right-to-Know Act (EPCRA), also known as Title III of the Superfund Amendments and Reauthorization Act (SARA), and EPA's implementing regulations (40 C.F.R. part 372). Releases of TRI-listed acrylates to all environmental media must be reported annually by facilities subject to the regulations. The TRI list can be found at 40 C.F.R. § 372.65. As of publication of this manual, Methyl Acrylate, Ethyl Acrylate and Butyl Acrylate are TRI-listed. [For additional information, see http://www.epa.gov/tri/index.htm]

Acrylates are also subject to the Hazardous Substance Inventory and hazard classification requirement of EPA's SARA §§ 311 and 312 programs and implementing regulations at 40 C.F.R. part 370). Acrylates generally meet the following characteristic categories for these programs: fire, reactive, acute health, and chronic health.

10.2.2 Discharges to Navigable Waters

Discharges to streams and other navigable waters are controlled under federal and state regulations, including the National Pollutant Discharge Elimination System (NPDES) (40 C.F.R. Parts 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, including site-specific effluent limitations. Non-compliance with these limitations or discharge without an effluent permit is subject to significant civil and criminal penalties. Similar laws may apply in other jurisdictions.

10.2.3 Discharges to Municipal Sewers

Discharges to public sewers and treatment works are regulated by national, federal, state and local regulations (including effluent limitations and any pre-treatment requirements), and by the specific permit conditions for the receiving treatment works.

No acrylates are normally 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 national, federal, state and local standards. In the United States, 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. Relevant implementing regulations can be found at 40 C.F.R. part 63. These rules define maximum achievable control technology (MACT) for emissions of Hazardous Air Pollutants (HAP) by source category. Ethyl Acrylate is listed as a HAP under Section 112 of the Clean Air Act; therefore, facilities that emit Ethyl Acrylate may be subject to these regulations. State or state-designated local authorities control sources of volatile organic compounds such as acrylates in order to achieve and maintain the National Ambient Air Quality Standard (NAAQS) for ozone. Ozone in the atmosphere is a result of volatile organic compounds reacting with nitrogen oxides in the presence of sunlight.

Regulatory authorities can require stringent controls for acrylate emissions because these acrylates have very low odor thresholds and can cause discomfort at low ambient air concentrations. Some regulations require vapor recovery or other emission abatement systems for bulk loading/unloading of volatile organic compounds. They may also require a fugitive emission monitoring program which involves inspection and maintenance of valves, pumps and compressors associated with the transfer of volatile organic compounds.

It is recommended to review all applicable governmental regulations to control air pollution to ensure compliance. The air pollution control divisions of most state environmental agencies may be able to provide guidance on standards which must be met and any permits or other operating authority which may be needed.

Keeping buildings used for processing or storage well ventilated helps prevent local accumulation of vapors and potentially toxic effects upon personnel. Ventilation methods include local exhaust and general dilution procedures. Local exhaust is most effective where vapors are emitted from local sources, such as liquid transfer points, pump houses and reactor areas. The method may involve operation within an exhaust hood or removal of vapors through ducts connected to an exhaust fan (*see Section 7.2 for specifications of electrical equipment*). General dilution ventilation may be used when vapors are emitted from scattered points throughout a storage or processing area. In this method, vapors are diluted and expelled by changing the air within the room or building. The ACGIH offers a publication entitled "Industrial Ventilation: A Manual of Recommended Practice". It is recommended to consult this manual for information on the design of exhaust hoods and ventilating equipment and recommended dilution air change rates. Whichever ventilation procedure is adopted, the level of vapors can be held to a minimum by keeping equipment in good tight repair and by confining all volatile materials.

The ventilated air may require odor abatement.

10.2.4.1 Removal of Acrylate Vapors from Contaminated Air

Vapors of acrylate monomer can be removed from air by scrubbing with a caustic and/ or an amine solution, combustion, adsorption on activated carbon, venting to a flare, incineration or a combination of these methods (*see Section 7.1.1*)

- Scrubbing with a Caustic Solution

Air streams contaminated with acrylate vapors can be purified by absorbing the vapors in aqueous sodium hydroxide and/ or amine solution. Additional information and advice is available from your supplier. Note that disposal of the spent scrubbing solution is regulated by national, federal, state and/or local authorities.

- Incineration

Acrylate vapors in exhaust air can be burned using flare stacks, thermal incinerators or catalytic incinerators. The choice of equipment is dependent upon the properties of the stream being treated as well as local permits and environmental regulations. It is recommended to consult the suppliers of the combustion equipment for design assistance.

- Absorption on Activated Carbon

Canisters of activated carbon can be used **BUT ONLY AFTER A SCRUBBING SYSTEM AS A BACK-UP OR FINISHING BED.** During the adsorption process, oxidation and evolution of heat may occur, which can raise the temperature of the adsorbent. At high acrylate concentrations, local overheating may ignite the system. For this reason, a flame arrester is normally installed between the storage tank and adsorption canisters. The activated carbon may be regenerated or disposed of after use. The disposal of the spent adsorbent is regulated by national, federal, state, and/or local authorities.

10.2.5 Releases to Land

Treatment and disposal of acrylates and mixtures containing acrylates are subject to federal regulations and state delegation of such regulation in the United States and may be subject to equivalent regulation in other countries. Disposal of acrylates or mixtures of acrylates on land is regulated by RCRA regulations, 40 C.F.R. Part 268, and may require permitting or prior treatment (*see Section 10.4*).

10.3 SPILL AND LEAK CONTROL

10.3.1 General Information

The primary emphasis is typically placed on the prevention of releases through careful design of equipment and sound operating procedures. If acrylates are lost from containment through a leak or spill use the proper personal protective equipment (*see* Section 5.5), decontamination procedures, and other safety considerations help ensure a safe and proper cleanup.

It is important to remember that spills of acrylates and materials contaminated by acrylates may need to be handled as hazardous wastes pursuant to RCRA or similar laws in other jurisdictions.

In the United States, a release of chemicals greater than the "reportable quantity" designated by EPA in CERCLA or SARA is reported immediately on 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 SDS for reportable quantity and pertinent phone numbers). The reportable quantity lists can be found at 40 C.F.R. part 302, Table 302.4 (CERCLA) and 40 C.F.R. part 355, Appendices A and B (SARA). As of publication of this manual, ethyl acrylate has a reportable quantity of 1,000 lbs under CERCLA.

10.3.2 Small Spills (Up To 4 Liters)

The use proper personal protective equipment can prevent exposure (*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. It is recommended to check with the operator of the treatment works prior to doing so. Otherwise, a suitable adsorbent can be used to pick up the spill. Solid phenothiazine (PTZ) may be added to the contaminated clean-up material to avoid polymerization and hence heat-up of the clean-up material. Contaminated adsorbent, any contaminated soil, and any supplies or personal protective equipment which cannot be decontaminated may have to be discarded as RCRA hazardous waste depending on the waste's characteristics or classification, per 40 C.F.R. Part 261 Subparts C and D (*see* Section 10.2.1).

10.3.3 Large Spills (Greater Than 4 Liters)

The use of proper personal protective equipment can prevent exposure (*see* Section 5.5). If the spill can be contained within a diked area, the material can be recovered in appropriate containers. It is strongly recommended to keep the material out of sewers (where it may create the danger of explosion) and surface waters (where it may cause contamination). Waste acrylates may polymerize, creating additional hazards (*see* Chapter 6). Avoiding mixing acrylates with incompatible materials or storing it in containers made of incompatible material helps prevent unintended polymerization, as noted in *Appendix A* (Incompatible Materials). In the event of accidental spillage of acrylate to surface waters or to a municipal sewer system, the appropriate pollution control and water supply agencies may have to be notified. There may also be reporting requirements under CERCLA and EPCRA/SARA (*see* Section 10.3.1). Floating booms are available for confining floating liquids and can be kept on hand where the possibility of spillage to surface waters exist to facilitate cleanup. With their use, the floating monomer can be pulled into a smaller area and skimmed off for recovery or disposal. Absorbing pads and other absorbents are useful for spills on the ground or surface waters and can also be kept on hand.

If contaminated dirt is classified as hazardous waste, RCRA rules determine its disposal or treatment in the US. In particular, land disposal restrictions under 40 C.F.R. Part 268 apply. Similar regulations may apply in other jurisdictions.

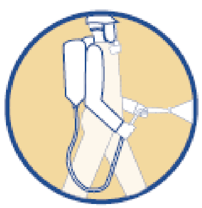
10.4 DISPOSAL OF WASTES

National, federal and/or local regulations regulate the disposal of acrylates, and they may need to be disposed of by a permitted waste facility. Direct disposal of these materials in a hazardous waste landfill may not be allowed. A preferred disposal route is incineration or burning for heat recovery in equipment which has had inspection and/or approval by the appropriate federal or state agency. Acrylate polymer may generally be disposed of in a permitted landfill or incinerated.

The destruction of aqueous waste streams containing dissolved acrylate by a biological digestion system which is part of a plant waste disposal system is a very satisfactory method. When such a system is properly operated, the danger of later contamination of public water supplies is eliminated. If a biological treatment plant is available, minor amounts of acrylate may be sparingly diluted with water and allowed to enter the treatment system after notification of the person in charge. Available data indicates the biodegradability of most acrylate materials in diluted form is good. Please refer to the SDS. Acrylates may however be toxic to the system if the bacteria have not been conditioned properly to this material. Accordingly, keeping the initial feed rate low with a stepwise increase helps condition the bacteria, if a significant amount is to be fed into the biological treatment purification. Due to the low odor threshold of most acrylates, sending material to an open waste treatment system may cause odor problems. As acrylates may be harmful to aquatic life, biological treatment is necessary and avoiding spillages into surface waters and public sewers prevents harm to aquatic life and ensures compliance with discharge regulations (see sections 10.2.2 and 10.2.3). Trickle filters are not recommended for disposal of these monomer wastes.

Though adequate dilution of concentrated wastes can reduce odor problems and fire hazard, direct disposal of dilute wastes to municipal sewage may still result in the pollution of drinking water. Acrylates impart a pronounced taste which may be detected at levels as low as 0.1 ppm. If poorly treated municipal sewage is discharged to a river or lake, a taste may thus develop in the water. Considering the final disposition of treated sewage and the method of treatment carefully before concluding that wastes may be safely added to public sewers can avoid taste issues. See your supplier SDS for RCRA classification and reportable quantities.

For disposing of waste materials originating from a laboratory or for retained samples, exercising great care to keep the monomer separated from incompatible materials (*see Appendix A*), e.g. peroxides, helps avoid unintended polymerization.



11 EMERGENCY RESPONSE

Signs of an emergency involving acrylates often involve increased temperatures (due to external heating or a exothermic polymerization) and venting or bulging of the container. **APPROPRIATE 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** (In Canada, call CANUTEC 1-888-226-8832). CHEMTREC or CANUTEC 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 acrylates normally develop written emergency plans for acrylate spills, fires, exotherms, and incipient polymerizations. These plans focus on clearly identifying the features that categorize an event as an emergency, what is done to secure the emergency site, and immediate actions to mitigate the danger. Two very important features of the plan are securing the area and early notification of CHEMTREC (or CANUTEC) 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 an acrylic ester storage system is installed and operated with all of the prevention measures recommended in this brochure and by prudent engineering practice, the chances of experiencing an inadvertent polymerization are minimized. However, in case of unforeseen events which might lead to incipient polymerization in a storage tank, detecting such an event in a timely manner can help avoid, stop, or mitigate polymerization. An option to provide additional protection from these unforeseen events is the use of a restabilization (shortstop) system. This subsection deals with the design and operation of a restabilization system as well as detection and response to polymerization. Please note that although shortstopping systems are optional, evaluating the risks for each facility associated with handling and storing acrylates helps determine the necessity for such a system.

11.1.1 Initiation Scenarios

Possible causes of acrylate runaway polymerizations are external overheating, removal of the dissolved oxygen from the monomer, over-aging, and chemical contamination.

If the monomer is purged with an inert (oxygen-free) gas (e.g., nitrogen or fuel gas) causing the dissolved oxygen to be 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 acrylate. If inert gas purging is known to have occurred, sparging the acrylate with a gas containing 5 to 21 Vol.-% of oxygen as soon as possible can prevent polymerization. Because it is readily available, air is preferred, but consideration must also be given to the flammability of the acrylate.

The scope of a contamination scenario is very difficult to pre-define because the identity and concentration of the contaminant are unpredictable. However, it is recommended that the restabilization (shortstop) system be immediately activated if contamination with a known or potential polymerization initiator has taken place. If such contamination has occurred without the knowledge of responsible personnel, activation of the restabilization (shortstop) system in the event of a polymerization exotherm, the detection of polymer, or the detection of the contamination can help prevent polymerization. Depending on the nature of the contamination, short stop may not be effective.

11.1.2 Polymerization Detection

The most common way to detect a polymerization is by monitoring the temperature of the tank contents. Redundant, remotely monitored temperature indicators with high temperature alarms are recommended. This allows the actual temperature to be compared to the "normal" storage temperature range. Acrylates are usually stored at ambient temperatures in tanks that do not have any special provisions for temperature control. Consequently, it is difficult to define the normal temperature range for stored acrylates. An abnormally high or increasing temperature can be an important indicator of polymerizing tank contents. What is "abnormal" is determined in the context of the tank's temperature history and perhaps the temperature of neighboring tanks. For instance, a product temperature of 90˚F during cold winter weather may be a warning sign of polymerization. The same temperature during hot summer weather or right after a transfer of warm acrylate into the tank might be quite normal. Additionally, commonly used temperature monitoring systems are 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. Thus, judgement is used in deciding whether a safety problem exists or not.

TEMPERATURES OF THE HIGH TEMPERATURE ALARM POINT (TYPICALLY AT OR SLIGHTLY ABOVE THE MAXIMUM RECOMMENDED STORAGE TEMPERATURE) OR HIGHER MAY INDICATE A HAZARDOUS SITUATION AND SHOULD BE IMMEDIATELY INVESTIGATED.

IF AT ANY TIME THE TEMPERATURE OF THE ACRYLATE REACHES 45˚C (113˚F) OR ABOVE OR HAS A RISE OF 2˚C (4˚F) PER HOUR, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300 (or in Canada CANUTEC at 888-226-8832).

An experienced chemical analyst may aid in the investigation by carrying out a soluble polymer test. The polymer test described in *Section 6.1.6* is of a qualitative nature. The absence of turbidity in this test is not normally interpreted as absolutely meaning that there is no polymerization reaction taking place. Even slow polymerization has the potential to accelerate into a runaway reaction. If the temperature rises above 45°C or the rate of rise is greater than 2°C per hour, and no source of external heat has been identified, this is typically considered an indication of polymerization. If the temperature rises at a rate greater than 5°C per hour or the temperature reaches 50°C, the situation is critical.

11.1.3 Restabilization (Shortstopping)

In developing an Emergency Response Plan, restabilization or shortstopping has been one method demonstrated to be effective in preventing or stopping polymerization in many situations.

Successful restabilization of acrylates 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) may vary depending upon the type of acrylate, temperature history, and the cause of the polymerization. Because of the large number of possible contaminants and concentrations of those contaminants, shortstopping may not be successful if the cause of the polymerization is contamination. The earlier short stop is added and mixed into the monomer the more likely it is to be successful in stopping the polymerization.

11.1.3.1 Restabilization (Shortstop) Inhibitor

Experimental evidence leads to the recommendation of phenothiazine (PTZ) as the preferred shortstop agent. Other anaerobic inhibitors such as 4-Hydroxytempo (4-HT) may also be effective - contact your supplier for any specific information. Any other materials (including MEHQ) used in this service may be ineffective. Phenothiazine is a solid, and for ease of mixing and addition, it is normally added as a solution. Commercially prepared solutions are available. While addition of PTZ has worked in most cases, there is no assurance that it will be effective in every case. Obvious exceptions are contamination of acrylates with large amounts of a polymerization initiator, or a delay in activation of the shortstop system.

Addition of a large amount of water to acrylates undergoing polymerization is not recommended. Although this will theoretically moderate the reaction by removing heat, the release of large volumes of steam and acrylate vapor, and the possibility of tank overflow, seriously detract from the efficacy of this option. Water is not soluble in acrylates, and it will likely sink to the bottom of the tank forming a second layer which will reduce its effectiveness in cooling a tank and take up space in the tank. Large amounts of water will significantly impact the solubility of PTZ. The lack of solubility can significantly impact its effectiveness as a short stop inhibitor. 4-HT is soluble in water and may be used in place of PTZ in some instances, but 4-HT tends to degrade in the presence of acid. Contact your supplier for specific recommendations.

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 is a good solvent for PTZ (preferably at least 6 wt percent PTZ solubility at the lowest anticipated ambient temperature) and miscible with acrylate.
- It is not viscous.
- It does not promote polymerization and is inert to the system.
- It is not highly toxic.
- It has low volatility so that it will not flash if the monomer heats up or if it is already hot and does not exacerbate any potential emission problem resulting from the emergency.

Another consideration may be the possibility of removing the solvent from the acrylate mixture after shortstopping. Examples of solvents used for shortstop PTZ are ethyl acetate, isopropyl acetate, N-methylpyrrolidone and tripropylene glycol. Contact your supplier for solvent recommendations.

The PTZ shortstop solution is typically 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, and to minimize the volume addition to the tank. The final desired concentration of PTZ in the acrylate to be shortstopped is typically 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 greater than 2°C (4°F) has been detected in one hour or less without external cause.
- There is an indication of instability or polymerization, including high temperature or detection of polymer. **MAKING A DECISION TO RESTABILIZE AT A LOW ENOUGH TEMPERATURE ALLOWS TIME FOR THE ADDITION AND MIXING OF THE INHIBITOR INTO THE TANK. IDEALLY THIS PROCESS WOULD BE ACTIVATED BEFORE THE TANK CONTENTS REACHES 50°C (122°F) .**
- There is a fire near an acrylates tank.
- A known polymerization initiator has been inadvertently added to the acrylates.
- The monomer is of excessive age and the decision has been made to dispose.

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 exothermic on-going polymerization. The lowest practical temperature or temperature rise is normally used as a call for investigation. Manual activation of the shortstop system is preferred for sites with continuous manning; otherwise, automatic activation of the shortstop system can be used. In either case, the shortstop system is typically activated if the criteria specified above are met.

UNDER NO CIRCUMSTANCES SHOULD ANYONE APPROACH A TANK WHOSE CONTENTS HAVE REACHED 60°C (140°F).

11.1.3.4 Mixing of Restabilization (Shortstop) Inhibitor

It is possible to quickly bring the concentration of the shortstop inhibitor to effective levels by circulating the tank contents with a pump[20] and/or by injecting a gas. If a pump is used to mix shortstop solution, designing its high temperature shutdown instrumentation (common deadhead protection feature) to accommodate the emergency procedure helps ensure its operability (detected high pump temperature intended for deadhead protection may prevent the pump from being used if the monomer has heated up due to polymerization). The use of eductor tubes on the tank inlet(s) or a gas lift can reduce the time required to mix the shortstop solution with the tank contents.

An important factor in the design and installation of the shortstop inhibitor system is the specific tank farm layout. The number of acrylate tanks, the location of diked walls and the types of chemicals within the diked areas are all considerations when planning a shortstop storage and distribution system. Having the shortstop system be capable of distributing adequate inhibitor to all the acrylate tanks which could be involved in a given incident, such as a fire in the containment area, ensures sufficient coverage of the shortstop. For multiple tank protection, 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 acrylates storage tanks, ancillary pump(s) may be necessary to transfer the PTZ solution from the inhibitor tank to the storage tanks. 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 tanks' recirculation lines. These options are best examined by plant personnel who are 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 acrylate storage tanks. It is an optional but commonly used safety enhancement. Shortstop inhibitor systems can vary in complexity and cost, and the design of any such system must be based on a careful risk analysis by the user. Your acrylate supplier can provide further information. Figures 11-1 and 11-2 represent two examples of shortstop systems. The key to symbols in Figures 11-1 and 11-2 is found in *Table 7-2*.

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

The delivery of shortstop inhibitor solution to the acrylate 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 gas supply source. The air/nitrogen mixture is used as a back-up source if the nitrogen system fails. The acceptability of nitrogen in this service is based on the fact that **PTZ DOES NOT REQUIRE THAT ACRYLATES 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 percent to 7 percent 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, isolating both the inert gas supply lines and the inhibitor solution tank minimizes solvent loss.

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

In Figure 11-2, the inhibitor solution is 50 wt percent PTZ dissolved in N-methylpyrrolidone[21]. 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 acrylates tank. The general steps for restabilizing an acrylates 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 acrylate tank using air or nitrogen (air is used in this example).
- After the shortstop tank is empty of inhibitor solution, the air will flow through the submerged nozzle at a moderate rate mixing the contents by the gas lift principle. The air flow rate is limited by an orifice located between the air cylinder and the pressure regulator.

Contact your supplier for further information on shortstop systems.

Figure 11-1: Acrylates Shortstop System Example I

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

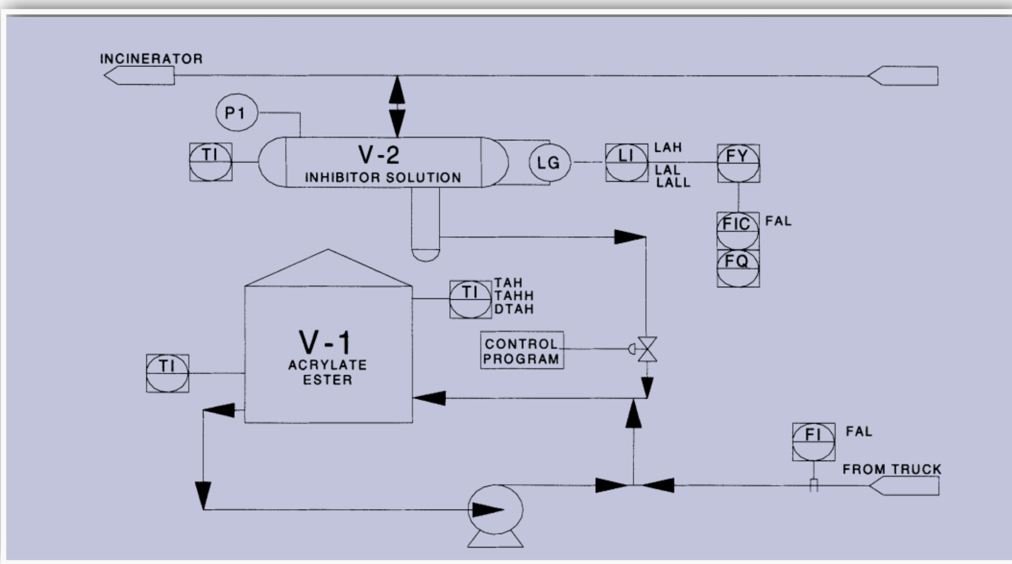
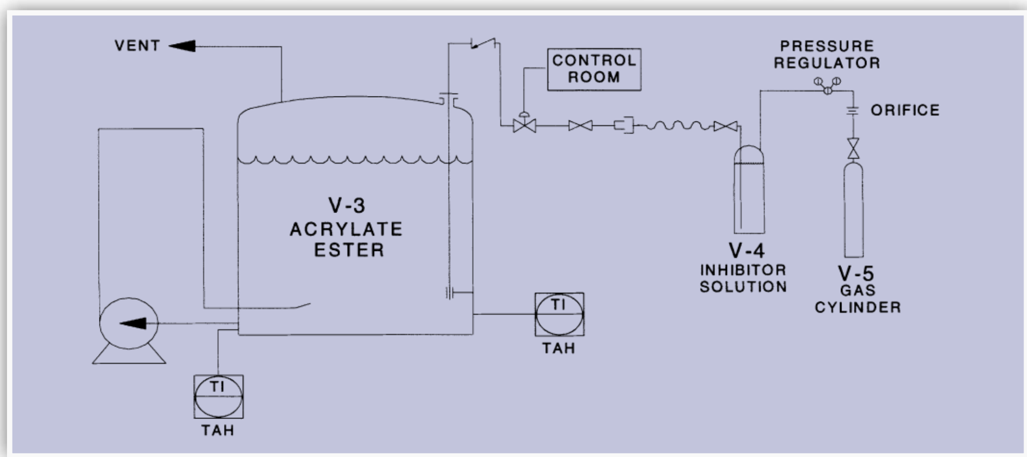


Figure 11-2: Acrylates Shortstop System Example II

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



11.2 SPILL CONTAINMENT

Containment is the most important technique for handling spills. Numerous techniques have been used successfully in containing spills: for material on the ground, diking, diverting and absorption; for material still in the leaking container, plugging, patching, repairing, tightening of container fittings or secondary containment (drums). More information on spills is given in *Section 10.3*.

11.3 FIRES

Methyl, Ethyl and i-Butyl Acrylates readily form flammable mixtures and Butyl Acrylate may form a flammable mixture with air at ambient temperatures. Protecting these acrylates from all potential sources of ignition prevents fires. Methyl, Ethyl, and i-Butyl Acrylates have flash points below 37°C (100°F) and are, therefore, classified as "FLAMMABLE" liquids by the National Fire Protection Association (NFPA) in the United States. The flash points of Butyl and 2-Ethylhexyl Acrylates are above 100°F but below 200°F, and they are classified as combustible liquids by the NFPA. However, Butyl Acrylate is classified as a "FLAMMABLE LIQUID" by DOT. Under fire conditions, rapid and uncontrolled polymerization can occur, resulting in an explosion. Vapors are heavier than air and may travel considerable distances to an ignition source and then flash back.

Acrylates are reactive materials which can polymerize if exposed to high temperatures. Therefore, emergency plans contain measures to closely monitor the temperature of acrylate storage tanks in fire situations. Provision for cooling to the storage tanks and evacuation of personnel may be warranted. Training of incident commanders, fire fighters, and emergency response personnel on the polymerization hazards of acrylates helps them determine the proper response in an emergency and prevents them from being impacted in case of a polymerization.

11.3.1 Procedures

Fire fighters are typically equipped with self-contained breathing apparatus (SCBA) and complete personal protective equipment, and applicable regulations and standards further specify legal requirements.

An acrylate storage tank fire or a fire in the vicinity of an acrylate storage tank is a very dangerous situation. If the acrylate reaches elevated temperatures, the liquid could polymerize. This could result in a violent reaction evolving considerable heat and pressure and ejecting hot vapor and polymer. Closely monitoring the temperature of the monomer during a fire situation helps prevent such a reaction. Quick response is essential for controlling and preventing escalation of the situation.

In the event of a severe fire with or near acrylates, when the liquid temperature reaches 50°C (122°F) evacuate all non-essential personnel to a safe distance from the tank because of the risk of a runaway polymerization. At 60°C (140°F) evacuate ALL personnel. Review *Section 11.1*, "*Detection And Response To Incipient Polymerization in A Storage Tank*" for additional understanding during fire response planning and drills.

In the event of a fire in the immediate vicinity of an acrylate storage container (tank, drum, truck, etc.), a typical response includes applying water spray or fog (deluge system, fire monitor, etc.) to the container's surface to absorb heat and maintain a lower temperature. This may also help disperse vapors prior to ignition. If the tank is uninsulated be aware that the ***external cooling will cause monomer vapors inside of the tank to condense which can pull a vacuum in the tank. If the vacuum protection vents are not sized for this scenario, the tank could be damaged or could collapse***. If an acrylate tank is insulated, taking caution when directing a spray onto it so can avoid destruction of the insulating material. Keeping a close watch on the temperature of the storage tank helps identify potential polymerization. If the temperature of the acrylate is rising despite the application of cooling water, it may be necessary to add a shortstopping agent**.** If the temperature of the acrylate equals or exceeds 50°C (122°F), then adding a shortstopping agent limits the risks of the acrylate polymerizing and escalating the situation. Shortstopping agents can be injected using one of the systems outlined in *Section 11.1.3.5* of this manual**. PLEASE NOTE THAT SHORTSTOPPING SYSTEMS ARE OPTIONAL, AND EACH FACILITY EVALUATES RISKS ASSOCIATED WITH HANDLING AND STORING ACRYLATES AND DETERMINES THE NECESSITY FOR A SHORTSTOPPING SYSTEM. WHEN LOCATING**

SHORTSTOPPING EQUIPMENT, CONSIDER AREAS THAT MAY BE IMPACTED BY A FIRE. CONSIDER LOCATING SHORTSTOPPING EQUIPMENT OUTSIDE OF THE IMPACT ZONE TO ALLOW FOR SAFE ACTIVATION OF THE EQUIPMENT IN THE EVENT OF A FIRE SCENARIO.

If the acrylate tank itself has caught fire, the first step generally is to add a shortstop agent as quickly as possible if it is safe to do so. This will help to prevent a runaway polymerization from occurring, assuming that this was not the cause of the fire.

Consult NFPA Standard 11 for the design of firefighting foam systems. After the fire, continuing to monitor the temperature of the storage tank for at least 48 hours helps verify that the temperature is dropping to ambient and the tank is stabilized.

11.3.2 Extinguishing Media

Typically, carbon dioxide or dry chemical are used for small fires and alcohol-resistant (AR-AFFF) foam or water fog for large fires. Acrylate and water are immiscible, and therefore water may be ineffective in extinguishing the fire; it can be used to keep fire-exposed containers cool. Addition of water to Butyl Acrylate or 2-Ethylhexyl Acrylate tanks could result in added venting of steam in the event that the tank temperature reaches 100°C (212°F) from either fire exposure or polymerization. Please note that water and/or foam is not normally added into a tank of burning acrylate 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 acrylate vapor.

11.3.3 Fire Prevention Suggestions

The following are general recommendations to prevent acrylate fires:

- Using non-combustible or fire-resistant area locations for acrylate monomer storage, handling and processing equipment.
- The risk of pool fires around acrylate tanks can be reduced by using diking design to separate other flammables from acrylate as much as is possible. If possible, separating flammable acrylates from other acrylates helps further reduce fire risk.
- Designing the floor of the containment area around acrylates tanks to slope away from the tank ensures a small pool fire will not be right next to the tank.
- Providing adequate venting for emergency conditions in vessels used for storage, handling and processing.
- Using proper electrical equipment and adequate grounding for static electrical discharge.
- Inspecting equipment and storage facilities regularly, especially vents and flame arresters.
- Correcting any leaks in equipment immediately.
- Providing adequate local exhaust and general ventilation in the working area and performing regular tests with a combustible gas indicator in any area where vapors might accumulate.
- Providing proper facilities to handle any accidental spillage.
- Using non-sparking tools for repair or service operations in any area which might contain combustible vapors.

Additionally, when evaluating procedures for shortstopping an unintended polymerization, consider the potential for static ignition created by charging dry inhibitor to acrylates by dropping through the vapor space.

12 REFERENCES

American Industrial Hygiene Association, “Odor Threshold for Chemicals with Established Occupational Health Standards,” 1995.

J. E. Amore and E. Hautala, “Odor as an Aid to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatiles for 214 Industrial Chemicals in Air and Water Dilution,” J. Appl. Toxicology, **3** (6), 272-290 (1983).

T. M. Hellman and F. H. Small, “Characterization of the Odor Properties of 101 Petrochemicals Using Sensory Methods,” J. Air Pollution Control Assoc., **24** (10), 979-982 (1974).

DIPPR values and references cited.

Kirk Othmer Encyclopedia of Chemical Technology, “Acrylic Acid and Derivatives,” 4th Edition, Release 2001.

Ullmann’s Encyclopedia of Industrial Chemistry, “Acrylic Acid and Derivatives,” 6th Edition, Release 2001.

Material Safety Data Sheet, Celanese Ltd., Dallas, Texas.

Odor threshold information for 2-Ethylhexyl Acrylate taken from: Basic Acrylic Monomer Manufacturers, Inc., “Basic Acrylic Esters: Background Information.”

Forsberg and Keith, Chemical Protective Clothing Performance Index, John Wiley & Sons, ISBN 0-471-32844-8. 10. Forsberg and Mansdorf, Quick Selection Guide to Chemical Protective Clothing, John Wiley & Sons, ISBN 0-471-28797-0.

Basic Acrylic Monomer Manufacturers, Inc., “Chemical-Protective Gloves for Acrylic Acid and Acrylic Esters,” Brochure, 1999.

L. B. Levy, J. Poly. Sci. Pt. A, **30**, 569-576 (1992).

Anon., I Chem E (U.K.), Loss Prevention Bulletin, Issue 126, 3-6 (1995); ibid., Issue 128, 27 (1996).

L. B. Levy, J. Poly. Sci., Poly. Chem. Ed., **23**, 1505-1515 (1985).

L. B. Levy, Plant/ Operations Progress, **6**, 188-189 (1987).

J. J. Kurland, J. Polym. Sci. Polym. Chem. Ed., **18**, 1139-1145 (1980).

L. B. Levy and M. B. Lakin, Process Safety Progress, 1**2**, 111-114 (1993).

C.A. Staples, S.R. Murphy, J.E. McLaughlin, H.-W. Leung, T.C. Cascieri, C.H. Farr, “Determination of selected fate and aquatic toxicity characteristics of acrylic acid and a series of acrylic esters”, Chemosphere, **40**, 29-38 (2000).

L. B. Levy and J. D. Penrod, Plant/ Operations Progress, **8**, 105-108 (1989).

P. D. Hoffman, AIChE Symposium Series No. 286, **88**, 77-82 (1992).

BASF Acrylate, “Emergency Restabilization with RESTAB Technology.”

M. J. Fried, “Stabilization of Acrylic Monomers”, Paint and Varnish,100, 604-609 (1994).

https://cameochemicals.noaa.gov/chemical/8349) USCG CHRIS Code BAI

APPENDIX A INCOMPATIBLE MATERIALS

Almost any contamination can potentially destabilize acrylates and avoiding such contaminants reduces the risk of unintended polymerization. The following is a partial list of chemicals which are incompatible with acrylates. 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

APPENDIX B ACRYLATE STORAGE & HANDLING SAFETY GUIDE

Acrylates are reactive chemicals and must be handled carefully during storage and when loading. This guide summarizes acrylate handling recommended "do's and don'ts". This guide can be used in conjunction with suppliers' SDS and *Acrylic Esters: A Summary of Safety and Handling, 4th Ed.* (to which this is an appendix).

HEATING OF ACRYLATES IS NOT REQUIRED OR RECOMMENDED FOR TRANSPORTATION OR STORAGE

WARNING:

If the temperature of the acrylates exceeds the recommended safe handling and storage temperature, (typically 35°C (95°F) – 40°C (104°F), or if an unexplained temperature increase of > 2°C (4°F) occurs, an emergency condition may exist.

IF AT ANY TIME THE TEMPERATURE OF THE ACRYLATE REACHES 45˚C (113˚F) OR ABOVE OR HAS A RISE OF 2˚C (4˚F) PER HOUR, AND NO SOURCE OF EXTERNAL HEAT HAS BEEN IDENTIFIED, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300 (or in Canada CANUTEC at 888-226-8832).

A decision to restabilize would normally be made at a low enough temperature to allow time for the addition and mixing of the inhibitor into the tank. Ideally this process would be activated before the tank contents reaches 50˚C (122˚F)

EXTREME DANGER:

UNDER NO CIRCUMSTANCES SHOULD ANYONE APPROACH A TANK WHOSE CONTENTS HAVE REACHED 60˚C (140˚F).

For prevention of dangerous polymerization and the safe handling and storing of acrylates, observe the following by:

- Not running pumps with outlet valves closed or blocked in.
- Not loading acrylates into an empty container (i.e., trailer, railcar, drum, etc.) if it is hotter than 100°F (38°C) or not loading "hot loads" over 40°C (104°F) next to an acrylate compartment, or acrylates next to a "hot load".
- Not using nitrogen or inert gas in contact with acrylates, but rather air or an air/nitrogen mixture that contains at least 5% oxygen. The inhibitor requires oxygen.
- Not contaminating acrylates with dirty hoses or by loading them into contaminated containers (vessels, trailers, railcars, totes, drums, etc.) Contaminated acrylates may violently polymerize and rupture the container or vessel.
- Not storing drums or totes in direct sunlight.
- Not inadvertently heating up or allowing acrylates to be heated up above normal recommended storage temperatures.
- Selecting the proper PPE for the job. Full protective clothing is typically considered as follows: a chemical resistant splash suit, gloves, boots, eye protection, and respiratory protection. Personal protective equipment (PPE) is selected based on the potential for exposure. (e.g., sampling, analysis, making & breaking connections etc.)
- Using Appropriate respiratory protection when exposure to acrylate vapors or mists may occur.
- Providing safety showers and eyewash facilities in close proximity to where acrylates are being handled
- If you get acrylates on you, rinsing with large amounts of water and getting immediate medical attention.
- Properly disposing of contaminated clothing, leather gloves and footwear.
- Note: Spilled acrylates are very slippery.

APPENDIX C ACRYLATE TRANSPORT SAFETY GUIDE

Acrylates are reactive chemicals and are handled carefully during storage and transit. This guide summarizes acrylate transportation recommended "do's and don'ts". This guide can be used in conjunction with suppliers' SDS and *Acrylic Esters: A Summary of Safety and Handling, 4th Ed.* (to which this is an appendix).

HEATING OF ACRYLATES IS NOT REQUIRED OR RECOMMENDED DURING TRANSPORT

WARNING:

If the temperature of the acrylates exceeds the recommended safe handling and storage temperature, (typically 35°C (95°F) – 40°C (104°F), or if an unexplained temperature increase of > 2°C (4°F) occurs, an emergency condition may exist.

IF AT ANY TIME THE TEMPERATURE OF THE ACRYLATE REACHES 45˚C (113˚F) OR ABOVE OR HAS A RISE OF 2˚C (4˚F) PER HOUR, AND NO SOURCE OF EXTERNAL HEAT HAS BEEN IDENTIFIED, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300. (or in Canada CANUTEC at 888-226-8832).

A decision to restabilize would normally be made at a low enough temperature to allow time for the addition and mixing of the inhibitor into the tank. Ideally this process would be activated before the tank contents reaches 50˚C (122˚F)

EXTREME DANGER:

UNDER NO CIRCUMSTANCES SHOULD ANYONE APPROACH A TANK WHOSE CONTENTS HAVE REACHED 60˚C (140˚F).

For prevention of dangerous polymerization and generally safe transport of acrylates, observe the following.

- Not running pumps with outlet valves closed or blocked in.
- Not loading trailers if they are hotter than 100°F (38°C).
- Not loading 'hot loads' (over 90°F (32°C)) next to an acrylate compartment or loading acrylates next to a "hot load".
- Not contaminating or inadvertently allowing acrylates to heat up or be heated up. (this can lead to unwanted onset of polymerization)
- Not contaminating acrylates with dirty hoses or loading them into contaminated containers (vessels, trailers, railcars, totes, drums, etc.)
- Contaminated acrylates may violently polymerize and rupture a vessel.
- Not storing drums or totes in direct sunlight.
- Not heating up or allowing acrylates to be heated
- WEARING PROPER PPE THAT HAS BEEN SELECTED FOR THE JOB
- When potential for exposure exists, full protective clothing is typically considered: a chemical resistant splash suit, gloves, boots, eye protection, and respiratory protection. Personal protective equipment (PPE) is selected based on the potential for exposure. (e.g., sampling, analysis, making & breaking connections etc.).
- Using appropriate respiratory protection used when exposure to acrylate vapors or mists may occur.
- Providing safety showers and eyewash facilities in close proximity to where acrylates are being handled
- If you get acrylates on you, rinsing with large amounts of water and getting immediate medical attention.
- Properly disposing of contaminated clothing, leather gloves and footwear.
- Note: Spilled acrylates are very slippery.

APPENDIX D ACRYLATE SAFETY GUIDE FOR EMERGENCY RESPONDERS

Acrylates are reactive chemicals and must be handled carefully during any emergency. This guide summarizes the most important recommended "do's and don'ts" regarding acrylates for emergency responders. This guide can be used in conjunction with suppliers' SDS and *Acrylic Esters: A Summary of Safety and Handling, 4th Ed.* (to which this is an appendix). The following are considerations for responding to an acrylate emergency:

- Protecting responders from exposure, fire, and polymerization hazards
- If it is safe to do so, establish temperature monitoring and obtain samples.
- If a sample analysis and/or temperature indicate shortstopping is needed, add and mix short stop inhibitor if it is safe to do so.
- If transloading is needed, avoid contamination, exposure to personnel, and spills. Ensure all equipment is clean and leak-free.

WARNING:

If the temperature of the acrylates exceeds the recommended safe handling and storage temperature, (typically 35°C (95°F) – 40°C (104°F), or if an unexplained temperature increase of > 2°C (4°F) occurs, an emergency condition may exist.

IF AT ANY TIME THE TEMPERATURE OF THE ACRYLATE REACHES 45˚C (113˚F) OR ABOVE OR HAS A RISE OF 2˚C (4˚F) PER HOUR, AND NO SOURCE OF EXTERNAL HEAT HAS BEEN IDENTIFIED, IMMEDIATELY NOTIFY CHEMTREC AT 1-800-424-9300. (or in Canada CANUTEC at 888-226-8832).

A decision to restabilize would be made at a low enough temperature to allow time for the addition and mixing of the inhibitor into the tank. Ideally this process would be activated before the tank contents reaches 50˚C (122˚F)

EXTREME DANGER:

UNDER NO CIRCUMSTANCES SHOULD ANYONE APPROACH A TANK WHOSE CONTENTS HAVE REACHED 60˚C (140˚F).

RECOGNIZING THE FLAMMABILITY HAZARD OF ACRYLATES

- Most acrylates are flammable. Protecting acrylates from ignition sources such as motor vehicles, combustion-engine powered equipment, spark-producing tools, and other sources of high temperatures prevents ignition.
- High temperatures may cause increased venting. Protecting vents from ignition sources helps reduce risk.
- Using fire protective PPE for emergency responders is recommended.

NOT USING PURE NITROGEN OR INERT GAS WITH ACRYLATES

- Acrylates require oxygen for the stabilizer to perform. Using air or an air/oxygen mixture that contains at least 5% oxygen in contact with acrylates ensures the polymerization inhibitor continues to function.
- Nitrogen may be used after acrylates have been stabilized with a minimum concentration of 200 ppm PTZ

RAPID ACRYALTE SELF-POLYMERIZATION MAY BE PREVENTED BY:

- Not contaminating stored acrylates with dirty hoses or loading them into contaminated containers. (vessels, trailers, railcars, totes, drums, etc.)
- Not moving acrylates from an emergency response site without adding PTZ stabilizer.
- Not combining acrylates with other chemicals without knowing the impact this combination will have on polymerization stability.

PERSONAL PROTECTION FOR EMERGENCY PERSONNEL

- Referring to the DOT Emergency Response Guide book (2016) Guide. Appropriate PPE for emergency response is typically a minimum of Level B (as defined by 29 C.F.R. § 1910.120, Appendix B).
- Decontamination of Personnel – by rinsing 15 to 20 minutes with large amounts of water & removing contaminated clothing, gloves and footwear.
- Decontamination of PPE/tools – by rinsing with large amounts of water with or without detergent

APPENDIX E THE DO'S AND DON'TS

THE DO'S AND DON'TS

For the safe use of Methyl Acrylate, Ethyl Acrylate, Butyl Acrylate and 2-Ethylhexyl Acrylate

DO	DON'T
Product Identification DO positively identify the product prior to use.	**Temperature/Heating** DON'T let temperature increase above 38 °C. DON'T heat while in storage or during transport.
Atmosphere DO ensure the presence of air (oxygen). Inhibitor (MEHQ) works only in the presence of oxygen.	**Atmosphere** DON'T handle under an inert atmosphere. Never use nitrogen.
Inhibition DO maintain good distribution of inhibitor & dissolved oxygen and observe the maximum time of storage.	**Contamination** DON'T contaminate (uncontrolled polymerization hazard).
Industrial Hygiene DO use the required Personal Protective Equipment. DO ensure good ventilation and wear respiratory equipment when working in poorly ventilated areas.	**Ignition Sources** DON'T forget grounding. DON'T fill product into a hot vessel, and do avoid all ignition sources.

Advice and help in acrylic acid and acrylic esters.

This poster is produced by the Basic Acrylic Monomer Manufacturers Group. All advice, information and guidance given is accurate to the best of the knowledge of BAMM and is given in good faith. However it remains at all times the responsibility of the reader / acrylic monomer user to ensure that this and other BAMM information and guidance materials apply to the intended situation or application. For further information please refer to the BAMM brochures (Safe Handling and Storage of Acrylic Acid/Acrylate Esters) and visit our website at www.bamm.net.

This poster is used with permission of European Chemical Industry Council (CEFIC) and the European Basic Acrylic Monomer Group (EBAM)

APPENDIX F ACRYLATE AUDIT AND ASSESSMENT PROTOCOL

The purpose of Appendix F is to provide a recommended Audit and Assessment Protocol for the basic Acrylic Esters or Acrylates – Methyl, Ethyl, iso-Butyl, Butyl, and 2-Ethylhexyl Acrylates inhibited with hydroquinone monomethyl ether (MEHQ, methoxyphenol), hereafter referred to as acrylates. The commercial acrylates or acrylic esters are typically stabilized with 10-20 parts per million by weight (ppm) of MEHQ. This audit and assessment protocol is an appendix to *Acrylic Esters: A Summary of Safety and Handling, 4th Edition* 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 AEed4.

ACRYLATE AUDIT AND ASSESSMENT PROTOCOL CONTENTS

ACRYLATE STORAGE

1. Storage Tank Design Characteristics *(refer to AEed4 Section 7.2 Design consideration)*

Conforming tanks used for acrylate storage to certain minimum design characteristics ensures safe storage.

1.1. Tanks in acrylate service are commonly constructed of steel, stainless steel, or baked phenolic-lined steel.

The most common tank design follows the American Petroleum Institute (API) standards. This design incorporates a vertical shell, a flat bottom and a conical top. Tanks can be constructed of steel, baked phenolic-lined steel or stainless steel.

Records Review

1.1.. Are tanks in acrylate service constructed of steel, stainless steel, or baked phenolic-lined steel?

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

1.2. A floating roof tank is not recommended for acrylate storage.

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

Records Review

1.2.. Do tanks used to store acrylates have floating roofs?

1.2.. If so, has the requirement for oxygen been considered in the design?

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

Separation of flammables from acrylates prevents pool fire risk around acrylate tanks.

Records Review

1.3.. Are dikes around storage tanks?

1.3.. Are the acrylates stored separately from other flammables?

1.3.. Is the floor of the containment area around acrylates tanks sloped away from the tank so a small pool fire will not be right next to the tank?

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

Records Review

1.4.. Are water monitors present? Coverage?

1.4.. Fixed water spray present?

1.4.. Is the vacuum protection adequate such that if the water spray causes vapors in the tank to condense the tank will not collapse?

1.5. The storage tank is typically equipped with vacuum and pressure relief valves unless the tank is open to the atmosphere. Relief of an unscheduled polymerization of an acrylate requires a weak seam roof or its equivalent.

Records Review

1.5.. Is the tank equipped with vacuum and relief valves?

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

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

Records Review

1.6.. Are safety showers and eyewash fountains present?

2. Preventing Gross Contamination (*refer to AEed4 Chapter 6 Instability and Reactivity Hazards & Appendix A Incompatible materials*)

Avoiding contamination of an acrylate with incompatible substances prevents unintended polymerization. Some chemicals can cause a sudden runaway exothermic reaction that can result in violent venting or rupture of the vessel. It is not practical to design a shortstop system to handle gross contamination incidents involving oxidizers, or free-radical-producing chemicals (*See AEed4 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. Positively identifying contents as the expected acrylate before offloading into the storage vessel improves safety. The preferred method of positive verification of the container contents is sampling the container at the receiving site for analysis.

Records Review

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

2.1.. Are there written procedures for this positive verification?

2.2. Almost any contaminant can potentially destabilize an acrylate and should be avoided. In most cases the compounds identified in AEed4 *Chapter 6* and *Appendix A* as incompatible materials will cause polymerization of the monomer. Having this list of incompatibles readily available at the site and be part of the regular training helps decrease the risk of contamination.

Records Review

2.2.. Is the list of incompatible materials readily available?

2.2.. Is the list of incompatible materials part of the regular training?

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

3. **Preventing Minor Contamination** ***(refer to AEed4 Chapter 6 Instability and Reactivity Hazards & Appendix A Incompatible materials)***

Contaminants can be introduced into an acrylate 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. Avoiding hard piping incompatible materials (i.e., caustics, oxidizers, free radical producers such as peroxides, azides, aldehydes, ethers, and others listed in AEed4 *Appendix A*) to an acrylate storage tank helps prevent contamination. Careful review of other tie-ins (vents, utilities, effluent, cleaning, instrument purges, heat transfer fluids, sparge gas, etc.) to the tank also helps prevent contamination of an acrylate with incompatible substances.

Incompatible materials can cause an i immediate or delayed, violent runaway polymerization.

Records Review

3.1.. Has a review been conducted to determine if there are contaminates hard piped (including inert gas) to an acrylate storage tank?

3.1.. 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 acrylate with incompatible substances?

3.2. Having a written procedure for both cleaning out an acrylate tank in preparation for modifications or inspection and returning an acrylate tank to service after internal tank

inspection/maintenance is performed decreases the likelihood of contamination (*AEed4 Chapter 8*).

Records Review

3.2.. Is there a written procedure for returning an acrylate tank to service after internal tank inspection/maintenance is performed?

3.2.. Is there a written procedure for the preparation and cleaning of acrylate tanks?

4. Monitoring Temperature (*refer to AEed4 Section 7.2.1 Temperature Control of Bulk Storage Tanks & Accessories*)

Monitoring the temperature of acrylates ensures the stability of the material during storage. Since temperature rises may indicate the onset of a polymerization reaction, temperature monitoring provides continuous indication of the stability of the acrylate. Early detection of a temperature rise helps prevent or inhibit the escalation of the incipient polymerization reaction to an uncontrolled violent reaction.

4.1. Acrylates are typically stored at ambient ~~a~~ temperature.

The common practice is to maintain acrylate storage tanks and piping systems at ambient temperatures (no heating or cooling). However, in some storage systems the acrylate is cooled in order to lower the vapor pressure.

Records Review

4.1.. Are the acrylates stored at ambient temperature?

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

4.1.. Although not typical or recommended, are there any heating or tracing sources on liquid lines in the storage and handling system?

4.1.. If so, are systems in place to limit heating medium temperatures to prevent spot polymerization initiation?

4.2. Storing most acrylates longer than the shelf life recommended by the manufacturer, typically one year from its production date, increases the risk of unintended polymerization.

Even if all the storage conditions outlined in AEed4 associated with temperature, inhibitor, dissolved oxygen, and contamination are met, acrylates are normally not be stored for longer than the manufacturer's recommended shelf life (typically one year) due to peroxide build-up. Peroxide is a polymerization promotor. Deviation from recommended storage conditions may significantly shorten the safe storage life.

Records Review

4.2.. Is there a system in place that assures that an acrylate is not stored longer than recommended shelf life?

4.3. The direct application of live steam, steam tracing, or steam coils to heat acrylates is typically avoided.

The common practice is to maintain acrylate storage tanks and liquid filled piping systems at ambient temperatures (no heating or cooling).

Records Review

4.3.. Are the acrylates heated?

4.3.. If so, why?

4.3.. What is temperature maximum of the heating medium?

4.3.. Is steam used to heat the acrylate?

4.4. Equip the acrylate tank with two or more temperature sensors that are continuously monitored remotely. The recommended setup is as follows:

- Each of the temperature sensors is independent and reliable.
- The temperature sensors are 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 are located with at least 90 degrees radial separation to measure temperatures in different regions of the tank.
- The temperature sensors are installed at a level that will always be submerged by the acrylate. A minimum level of liquid is maintained per site-specific standard operating procedures (SOP).

Records Review

4.4.. Are the acrylate tanks equipped with two or more temperature sensors that can be continuously monitored by personnel remotely?

4.4.. Do drawings reflect two temperature sensors that have 90 - 180 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.. Are the temperatures independent and reliable?

4.4.. Are the temperature indicators submerged at all times there is liquid in the tank?

4.4.. Is there an SOP that defines the minimum level of liquid in the tank?

4.5. Installing alarms to alert personnel if any temperature sensor detects an abnormally high temperature helps improve the response to potential polymerization.

- A high temperature alarm is typically set slightly above maximum recommended storage temperature.
- Temperatures equal to or greater than 40°C/104°F are normally investigated immediately
- A Hi-Hi alarm is typically set no higher than 45 °C/113°F.
- A written procedure that describes the response to temperature alarms, and personnel training on that procedure, help improve response to potential polymerization.
- A "Rate of Temperature Rise" detection system is recommended if equipment allows (*see AEed4 Section 11.1.3 Restabilization (Shortstopping))*

The high temperature alarm indicates that acrylate 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.

Records Review

4.5.. Do the acrylate tanks contain alarms that are set:

- High temperature, no higher than 40°C/104°F?
- HI-Hi temperature, no higher than 45 °C/113°F?

4.5.. Is there a written procedure that describes the response to temperature alarms?

4.5.. Are personnel trained on the procedure for response to temperature alarms?

4.5.. Are temperatures above 40°C/104°F investigated immediately?

4.6. Continuous circulation of tank contents through a properly designed eductor ensures good mixing.

- It is recommended to maintain circulation.
- The circulation return line typically contains an eductor(s).

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

Records Review

4.6.. Is the circulation maintained on the tank?

4.6.. Does the circulation return line contain an eductor?

5. Controlling Dissolved Oxygen (*refer to AEed4 Chapter 6 Instability and Reactivity Hazards & Chapter 7 Bulk Storage Facilities and Accessories*)

The acrylates are inhibited with monomethyl ether of hydroquinone (MEHQ). MEHQ stabilizes the acrylate with respect to polymerization ONLY if dissolved oxygen is present.

5.1. Acrylates are stored under a blanket atmosphere containing 5 to 21 Vol.-% oxygen 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.. Is there a system in place to assure that the acrylate is stored under a blanket atmosphere that contains 5 to 21 Vol.-% oxygen?

5.2. Protection of any gas blending system used to generate a reduced-oxygen atmosphere for acrylate service with high and low oxygen concentration alarms helps ensure a controlled gas composition. The layers of protection may be either oxygen analyzers or a ratio of flow meters.

Records Review

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

5.3. Acrylates in storage are typically circulated through a properly designed eductor(s) to replenish the dissolved oxygen by contact with the blanket gas.

Records Review

5.3.. Does the tank have an eductor?

5.3.. Is there a system in place to ensure interruptions in circulation are corrected promptly?

5.4. Maintaining a minimum of 10% outage in acrylate tanks helps provide adequate oxygenation.

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

Records Review

5.4.. Is a minimum of 10% outage maintained in acrylate tanks?

5.4.. Is there a high-level alarm at 90% or lower?

5.5. An inert gas (one containing less than 5 volume % oxygen) is not recommended to be used in acrylate service. Specific examples include the following, which are not recommended:

- Inert gas as blanket gas or as barrier gas for dual seal pumps.
- Inert gas as motive gas for making transfers, blowing lines, pigging lines, etc.
- Inert gas for sparging an acrylate tank, or for purging a vessel or instrument line to be used in acrylate service.
- Inert gas hard-piped to an acrylate tank.

Any inert gas in contact with an acrylate can potentially defeat the MEHQ-oxygen inhibitor system.

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

Records Review

5.5.. 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.. Is inert gas used for sparging acrylates or for purging a vessel or instrument line to be used in acrylate service?

5.5.. Is inert gas hard piped to an acrylate tank?

5.6. In case of inadvertent purging of an acrylate with an inert gas, sparging the acrylate with air or blended gas with 5-21% oxygen as soon as possible can restore dissolved oxygen levels.

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

Records Review

5.6.. Is there a procedure in place so that, in the case of inadvertent purging of an acrylate with an inert gas, the acrylate is sparged with oxygen containing gas as soon as possible?

6. Ensuring Inhibition (*refer to-AEed4 Chapter 6 Stability and Reactivity Hazards*)

Storage of un- or under-inhibited acrylates is not recommended. Commercial grade acrylates are typically inhibited with aerobic inhibitors, such as MEHQ. The producer's product specifications include the type and minimum concentration of the inhibitor. Acrylates stored under conditions described in this minimum standard typically have a stability time of one year. MEHQ stabilizes the acrylates only if dissolved oxygen is present.

6.1. Acrylates normally contain a minimum of 10 ppm of MEHQ inhibitor .

Even if all the conditions of this standard associated with temperature, inhibitor, dissolved oxygen, and contamination are met, storing acrylates for longer than one year is not recommended due to peroxide build-up. Differing storage conditions may significantly shorten the safe storage life.

Records Review

6.1.. Is there a process in place to ensure that the acrylate contain a minimum of 10 ppm of MEHQ inhibitor?

6.1.. Is there a process in place to ensure that the acrylate is not stored for longer than one year?

7. Shortstopping Incipient Runaway Polymerizations (*refer to AEed4 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. Addition of phenothiazine (PTZ) can be effective at stopping a polymerization reaction.

7.1. It is recommended that all acrylate storage tanks have a plan for shortstopping incipient runaway polymerizations.

Records Review

7.1.. Do all acrylate storage tanks have a plan for shortstopping incipient runaway polymerizations?

7.2. The initial concentration of PTZ in the shortstop solution is typically not higher than the solubility limit in the solvent at the minimum expected winter ambient temperature. It is recommended to analyze charges of the shortstop solution on receipt to verify the design concentration, and to check them periodically.

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

Records Review

7.2.. 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.. Is the shortstop solution analyzed on receipt to verify design concentration?

7.2.. Is the PTZ concentration checked periodically?

7.3. Designing the shortstop system to deliver PTZ solution to achieve a final concentration of PTZ in the acrylate tank in the range of 200 to 1000 ppm helps ensure the shortstop is effective.

Records Review

7.3.. Has a mixing analysis been done to ensure the system as designed will result in a final concentration of PTZ in the acrylate of at least 200 PPM?

7.4. Product temperatures of 40°C/104°F or higher can be hazardous and are normally immediately investigated.

Investigation includes determining the cause for the abnormally high temperature and correcting that cause. Failure to correct could jeopardize the stability of the acrylate and necessitate emergency response

Records Review

7.4.. Are procedures in place to initiate an investigation if the temperature of stored acrylate reaches 40°C/104°F or higher?

7.5. Typical criteria for the addition of shortstopping inhibitor include:

- A temperature rise greater than 2˚C (4˚F) has been detected in one hour or less without external cause.
- There is an indication of instability or polymerization, including high temperature or detection of polymer.
- There is a fire near an acrylates tank.
- A known polymerization initiator has been inadvertently added to the acrylates.
- The monomer is of excessive age and the decision has been made to dispose.

Records Review

7.5.. Is the shortstop procedure activated whenever there is a temperature rise exceeding 2˚C (4˚F) in one hour or less, for no known reason?

7.5.. Is the shortstop procedure activated whenever there is an indication of instability or polymerization, including high temperature or detection of polymer?

7.5.. Is the shortstop procedure activated whenever there is a fire near the acrylate tank?

7.5.. Is the shortstop procedure activated whenever a known polymerization initiator has been inadvertently added to the acrylates?

7.5.. Is the shortstop procedure activated whenever the monomer is of excessive age and the decision has been made to dispose?

7.6. Having a written procedure for activation of the shortstop system, and training personnel periodically on that procedure, helps improve the response to a potential polymerization event.

Records Review

7.6.. Is there a written procedure for activation of the shortstop system?

7.6.. Are people trained periodically on the written procedure for activation of the shortstop system?

7.6.. Is the system kept evergreen by periodic testing and dry runs (equipment, procedures, and shortstop analysis)?

8. Pumps, Piping, Miscellaneous *(refer to AEed4 Chapter 7 Bulk Storage Facilities and Accessories)*

Proper design of ancillary systems on an acrylate tank contributes to the safe storage and handling of the acrylates. Conforming the pumps used to circulate and transfer acrylates to minimum design standards ensures safety of the system. It is recommended to design piping systems used in conjunction with acrylate storage tanks to minimize the possibility of inadvertent polymerization and oxygen-stripping. The use of proper materials of construction for pump seals, gaskets, and hoses further improve acrylate stability. (*AEed4 Section 7.2.8*)

8.1. All pumps and piping in acrylate service are typically dedicated to the acrylate service and constructed from steel or stainless steel.

Other materials of construction might be acceptable, but need to be carefully reviewed to determine impact on acrylate stability.

Records Review

8.1.. Are all pumps and piping in acrylate service dedicated to acrylate service and constructed from steel or stainless steel?

8.2. It is recommended to instrument acrylate pumps to protect against "deadhead" (or blocked-in) situations, and to have pump deadhead protection present to reduce the risk of blockage which can lead to unintended polymerization.

Records Review

8.2.. Are acrylate pumps instrumented to protect against "deadhead" situations?

8.3. Not connecting incompatible materials (i.e., caustics, oxidizers, free radical producers such as peroxides, azides, aldehydes, ethers, and others listed in AEed4 *Appendix A*) to a dedicated acrylate line helps avoid contamination. Carefully reviewing other tie-ins (vents, utilities, effluent, cleaning, instrument purges, heat transfer fluids, sparge gas, etc.) to dedicated acrylate lines also helps prevent contamination of acrylates with incompatible substances.

Incompatible materials can cause an immediate, violent runaway polymerization.

Records Review

8.3.. Has a review been conducted to determine if there are contaminates hard piped to a dedicated acrylate line?

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

8.4. Tracing is not normally used on acrylate circulation and transfer lines or pumps.

Freeze protection is not required for acrylates; tracing may become of source of inadvertent heat buildup which may lead to unintended polymerization.

Records Review

8.4.. Is tracing used on acrylate circulation lines, transfer lines, or pumps?

8.5. Ensuring acrylates never come into contact with any gas containing less than 5% oxygen helps maintain efficacy of the inhibitor. ***See Section 7.1 of AE~~A~~ed4***

Records Review

8.5.. Does the acrylate contact any gas containing less than 5% oxygen?

DISTRIBUTION OF ACRYLATES

Acrylates are typically transported in rail tank cars (T/C) or 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 AEed4 Chapter 9*)

Conforming shipping containers used for acrylate transportation to certain minimum design characteristics ensures safety.

Bulk shipping containers (T/C and T/T) in acrylate transportation service are typically constructed of steel, stainless steel or aluminum. Drums used for acrylate transportation are typically steel drums or steel drums with phenolic internal coating Totes are normally constructed of HDPE, stainless steel or aluminum. Proper gaskets are used. (*see* Section 7.2.11)

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 acrylate stability? Does packaging protect product from UV exposure?

9.1.. Tank Cars (T/C)

9.1.. Tank Trucks (T/T)

9.1.. Totes (IBC)

9.1.. Drums

10.* Preventing Gross Contamination** ***(reference AEed4 Chapter 6 Stability and Reactivity Hazards & Appendix A (Incompatible materials) & Chapter 9 Safe Transport of Acrylates)

Avoiding contamination of an acrylate with an incompatible substance helps prevent polymerization. Some chemicals can cause a sudden runaway exothermic reaction that can result in violent venting or possibly an explosion of the vessel.

11. Before a shipping container can be loaded with an acrylate, ensuring that the container is clean or that the last contents were an acrylate helps prevent contamination.

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

Records Review

11.1.. Is there protection to ensure that the container is clean or that the last contents were an acrylate?

11.1.. If dedicated shipping vessels are used, have procedures at receiving end been checked to ensure that contamination is avoided?

11.2. Before a product is transferred, it is recommended to confirm the identity of the product. One method would be a positive verification of the container contents by sampling at the receiving site. it is recommended to document these procedures in writing.

Records Review

11.2.. Is protection against contamination employed before an acrylate is transferred?

1.1.1. Is positive identification of contents required?

1.1.2. Is there a written SOP?

2. Preventing Minor Contamination (*refer to AEed4 Chapter 6 Stability and Reactivity Hazards & Appendix A Incompatible materials)*

Acrylate shipments can become contaminated from:

- heels of previous cargoes
- inadequate cleaning
- contaminated hoses and pumps
- vent line over-pressuring
- co-mingling vent lines of incompatible products
- errors during the loading process
- excess rust
- other possible causes.

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

2.1. Using new drums used for shipping acrylates prevents contamination. Metal totes used for shipping acrylates are recommended to be new, dedicated, or cleaned. Totes made of HDPE are recommended to be new or dedicated to acrylate service.

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

Records Review

2.1.1. Are new drums used for shipping acrylates?

2.1.2. Are metal totes new, dedicated or cleaned?

2.1.3. If totes are made of HDPE, are they new?

2.2. Not allowing incompatible materials (i.e., caustics, oxidizers, free radical producers such as peroxides, azides, aldehydes, ethers, and others listed in Acrylic Esters *A Summary of Safety and Handling* *Appendix A* to come into contact with the acrylates during the loading process or in the transport container prevents contamination.

Carefully reviewing tie-ins to the loading system lines (vents, vent scrubbers, utilities, effluent, cleaning, instrument purges, heat transfer fluids, sparge gas, etc.) also helps prevent contamination of the acrylate with incompatible substances.

Incompatible materials can cause an immediate, violent runaway polymerization.

Records Review

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

2.3. Having written cleaning procedures for T/Ts, T/Cs, and totes can 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

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

2.4. Keeping acrylates in their shipping container beyond one year from its production date is not recommended.

If an acrylate has been in a shipping container beyond one year, it is typically 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 AEed4 associated with temperature, inhibitor, dissolved oxygen, and contamination are met, acrylates generally do not remain in the shipping container for longer than one year due to peroxide build-up. Not meeting all the recommended storage conditions may significantly shorten the safe storage life.

Records Review

2.4.1. Is the acrylate stored in a shipping container for longer than one year?

2.4.2. If stored for longer than one year, has product been scheduled for disposal or rework and has at least 200 ppm PTZ added?

3. **Monitoring and Controlling Temperature** ***(refer to AEed4 Chapter 9 Safe Transport of Acrylates & Section 7.2.1 Bulk Storage Facilities and Accessories)***

3.1. Avoiding the direct application of live steam in tracing or coils on liquid filled lines prevents excessive heating and polymerization.

There is no practical way to limit and control the temperature of steam below the maximum allowed temperature for the heating medium.

Records Review

3.1.1. Is live steam used to heat acrylates?

3.2. There is no need to heat acrylates in transit.

If the temperature of acrylate containers is discovered to be significantly greater than the ambient temperature around them at any time during the distribution process, it could be an indication the contents are undergoing an inadvertent polymerization. Hence, the responsible party (e.g., carrier or customer) should immediately notify CHEMTREC (1-800-424-9300) (or in Canada CANUTEC at 888-226-8832).

. 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

3.2.1. Are expected storage temperature ranges well defined?

3.2.2. Is there a documented system in place to notify CHEMTREC if product temperature is higher than expected?

4. **Controlling Dissolved Oxygen (*refer to AEed4 Chapter 9 Safe Transport of Acrylates, & Chapter 7 Bulk Storage Facilities and Accessories)***

Typically, acrylates are inhibited with monomethyl ether of hydroquinone (MEHQ). MEHQ stabilizes the acrylate with respect to polymerization ONLY if dissolved oxygen is present.

4.1. Transportation containers (T/C, T/T, totes and drums) contain a blanket atmosphere containing at least 5 volume % oxygen prior to being loaded with acrylates. This can be

achieved by a gas blending system with the proper controls or by air. Dry, oil-free air is preferred.

Records Review

4.1.1. Does the transportation container contain a blanket atmosphere of at least 5% oxygen prior to loading acrylates?

4.2. An inert gas (one containing less than 5 volume % oxygen) is not recommended to be used when shipping acrylates. Some specific examples include the following, which are not recommended:

- 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 an acrylate can potentially defeat the MEHQ-oxygen inhibitor system.

Records review

Is an inert gas used when shipping acrylates in any of the following:

4.2.1. Blanket gas in the shipping container?

4.2.2. Motive gas for making transfers?

4.2.3. Motive gas for blowing lines?

4.2.4. Motive gas for pigging lines?

4.2.5. Motive gas for clearing lines?

4.2.6. Purge gas for shipping containers?

4.2.7. Barrier gas for dual seal pumps?

4.3. In case of inadvertent purging of an acrylate with an inert gas, sparging the acrylate with a gas containing greater than 50% oxygen as soon as possible can restore dissolved oxygen.

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

Records Review

4.3.1. If an acrylate is inadvertently purged with an inert gas is the acrylate sparged with a gas containing more than 5% oxygen as soon as possible?

5. Responding to Runaway Polymerization Incidents (*refer to AEAed4 Section 11.1 Detection and Response to Incipient Polymerization in a Storage Tank & Chapter 9 Safe transport of Acrylates*)

5.1 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) (or in Canada CANUTEC at 888-226-8832). **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

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

5.2. PTZ, preferably dissolved in a suitable solvent, is typically stored at each transloading site. Adding PTZ before the container temperature reaches 50 °C/122°F if polymerization is suspected helps ensure its effectiveness. PTZ is added to a container when a known incompatible contamination has occurred.

A. Records Review

5.2.1. Is PTZ stored at the transloading site?

5.2.2. Is PTZ added before the container temperature reaches 50 °C/122°F if polymerization is suspected?

5.2.3. Is PTZ added when a known incompatible contamination has occurred?

5.2.4. Has the amount of PTZ or PTZ solution been calculated for container size?

6. Pumps, Piping, Miscellaneous (*refer to AEed4 Section 7.2 Design Considerations & Chapter 9 Safe Transport of Acrylates*)

Proper design of ancillary systems used during loading/unloading contributes to the safe handling of acrylates during shipment. Conforming the pumps used to transfer acrylates to minimum design standards helps ensure safety. Hoses used in conjunction with acrylate loading/unloading operations are typically designed to minimize the possibility of inadvertent polymerization

6.1. Dedicating all pumps and hoses in acrylate service to acrylate service or properly cleaning them prior to use for acrylate service reduces the risk of contamination. Pumps are typically constructed of stainless steel.

DOT regulatory requirements, and similar requirements in other countries, call for constant attention during offloading/loading operations.

Records Review

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

6.1.2. Are pumps and hoses constructed of proper materials?

6.2. Steam tracing is not normally used on acrylate loading/unloading hoses, pipes, or pumps.

Records Review

Is steam tracing used on acrylate loading/unloading hoses, pipes or pumps?