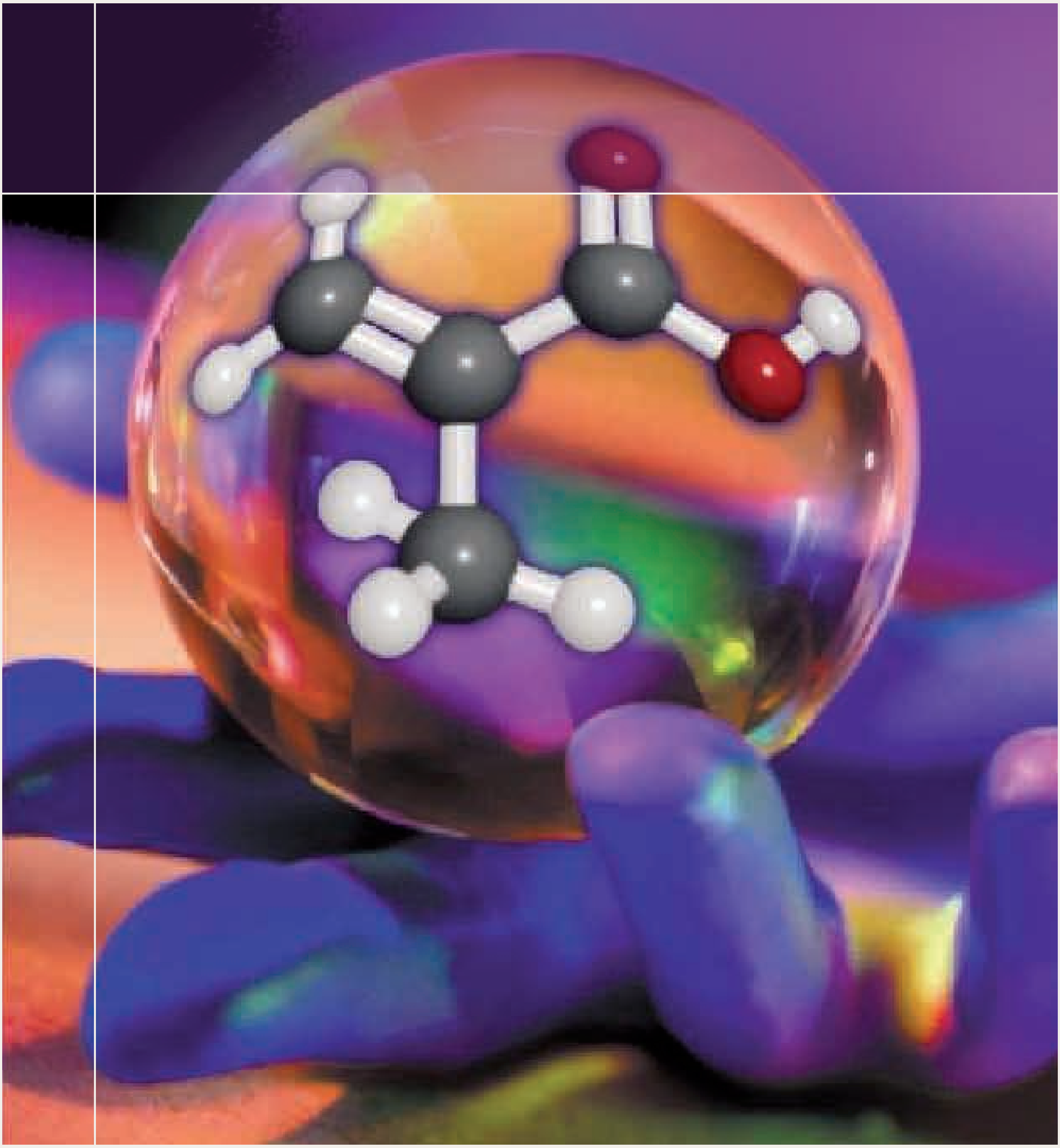
Methacrylic Acid
Safe Handling Manual



Introduction

This Manual provides general information on the safe handling of methacrylic acid and dealing with specific hazards in an appropriate manner. These hazards include health risks, environmental risks, and the potential of uncontrolled polymerization.

Properties and characteristics quoted in this Manual refer to methacrylic acid with a minimum content of 99 percent pure. They conform to specifications reported in the technical information bulletins issued by methacrylic acid manufacturers. Some of the physical data might be subject to minor changes due to variable concentrations of natural impurities.

Please read this entire Manual before handling methacrylic acid or before designing a storage system for methacrylic acid. All preventive measures described in this Manual must be followed to minimize the risks associated with this substance.

Preface

This Manual is a publication of the Methacrylate Producers Association, Inc. (MPA) and the Methacrylates Sector Group of the European Chemical Industry Council (Cefic) and represents industry best practice. It provides general information to methacrylic acid users about the unique hazards associated with handling this chemical and measures to be followed to protect human health, equipment, and the environment. Methacrylic acid hazards include its corrosivity, combustibility, and its potential for unanticipated, uncontrolled, and rapid polymerization. Read and familiarize yourself with this entire Manual before using the information it contains. Also, thoroughly review your supplier's Material Safety Data Sheet for methacrylic acid before working with it. Additional information is available in the publication entitled "OECD SIAR Methacrylic Acid (CAS No. 79-41-4)", 2003. If you have any questions or need more detailed information, you should contact your methacrylic acid supplier.

This Manual was prepared by the following companies that are members of MPA and/or Cefic: BASF SE (European Union), CYRO Industries (United States), Arkema Inc. (United States), Arkema France (France), Lucite International (United States, United Kingdom), Repsol YPF Química, S.A. (Spain), Rohm and Haas Company (United States) and Evonik Röhm GmbH (Germany).

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Although MPA and Cefic believe that the information contained in this Manual is factual, it is not intended as a statement of legal requirements with respect to handling methacrylic acid. Consult with legal counsel and/or appropriate government authorities to ensure compliance with local, regional, national, and international laws and regulations.
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Table of Contents

1 Names

Chemical Name	Methacrylic acid
Common Name	Methacrylic acid
Synonyms	2-Methacrylic acid
	α-Methyl acrylic acid
	2-Propenoic acid, 2-methyl
	2-Propenoic acid, α-methyl
CAS Registry Number	79-41-4
EINECS Number	201-204-4
Chemical Formula	$CH_2=C(CH_3)COOH$
UN Number	2531
IMDG-/ICAO-Class	8
ADA/RID Orange plate	89/2531
ADR/RID-Classification	8

2 Properties of Methacrylic Acid

2.1 Grades of Methacrylic Acid

Glacial methacrylic acid is a refined grade of methacrylic acid and contains monomethyl ether of hydroquinone (MEHQ, CAS 150-76-5) as its inhibitor. Note that MEHQ is also known as para-methoxyphenol (PMP) and 4-Hydroxyanisole (HA). Grades are available with different levels and types of inhibitor. Specific information is available upon request from producers.

2.2 Properties and Characteristics of Glacial Methacrylic Acid

The following values were taken from DIPPR (Design Institute for Physical Properties) where possible. DIPPR is a subsection of AIChE and specializes in compiling physical property data banks for various chemicals. The following is the most current information at the time of publication. Contact a producer for more up-to-date information or more detailed information about the properties of the grade of methacrylic acid.

PROPERTIES	VALUES/INFORMATION	NOTES
Molecular Weight	86.09	G1
Physical State	Liquid above 15°C (59°F)	G1
Odor	Sharp, acrid, detectable at approx. 0.2 ppm	F
Color	Clear and colorless	
Solubility in Organic Solvents	Soluble in most solvents	
Light Sensitivity	Light promotes polymerization	
Hygroscopicity	Very hygroscopic	
Water Solubility	Totally miscible above 16°C (61°F)	F
Flammable Limits % by volume in air at 760 mm Hg minimum oxygen, calculated, %	1.6 (LEL), 8.7 (UEL) 7.2	G1 C12
Flash Point, Tag Closed Cup, DIN 51758 Abel-Pensky, EN 22719	67°C (153°F) 77°C (171°F)	G1 G2
Autoignition Temperature, approximate	435°C (815°F)	G1
Freezing Point, BS 523:1964	15°C (59°F)	G1
Vapor pressure, at 20°C (68°F), mbar (mmHg) *at 40°C (104°F), mbar (mmHg)* *at 60°C (140°F), mbar (mmHg)* *at 100°C (212°F), mbar (mmHg)* *at 120°C (248°F), mbar (mmHg)*	*0.89 (0.67)* *3.95 (2.96)* *14.2 (10.6)* *109.7 (82.3)* *250.6 (188)*	G1

PROPERTIES	VALUES/INFORMATION	NOTES
Boiling Point, at 760 mm Hg (1013 mbar), DIN 51751 *at 50 mm Hg (67 mbar), DIN 51751* *at 10 mm Hg (13 mbar), DIN 51751*	161°C (322°F) *90°C (194°F)* *60°C (140°F)*	G1
Equilibrium Concentration in air, calculated *at 20°C (68°F), ppm (mg/m³)* *at 25°C (77°F), ppm (mg/m³)* *at 30°C (86°F), ppm (mg/m³)*	 *878 (3369)* *1300 (4988)* *1905 (7309)*	G1
Critical Volume, L/mol (ft³/lb-mole)	0.28 (4.49)	G1
Critical Pressure, mbar (psia)	47900 (695)	G1
Critical Temperature, °C (K)	389 (662)	G1
Specific Gravity at 20°C (68°F), g/cm³, DIN 53169	1.014	G1
Liquid Coefficient of Thermal Expansion, units of specific gravity/°C	0.0009786	G3
Specific Gravity of Vapor (air = 1)	2.97	C13
Liquid Viscosity at 20°C (68°F), cp (mpas)	1.54	G1
Surface Tension at 20°C (68°F), mN/m	65.9	G2
Heat of Combustion at 25°C (77°F), kJ/kg	23000	G1
Heat of Vaporization, kcal/mol (kJ/mol)	9.6 (40.2)	G1
Heat of Fusion, kcal/mol (kJ/mol)	1.926 (8.0625)	G4
Heat of Polymerization, kJ/kg	768	G5
Heat of Neutralization, kJ/kg	660	U
Specific Heat, at 20°C (68°F), kJ/kg, K *at 100°C (212°F), kJ/kg, K*	1.86 *2.02*	G1
Dissociation Constant at 25°C (77°F)	2.19×10^{-5}	G6
Electrical Conductivity (range of estimates), mho/cm²	$4\text{-}10 \times 10^{-5}$ (0%-0.8% H_2O)	F
Refractive Index, n_D^{25} n_D^{20}	1.4288 *1.4314*	G1, 7 *G8*
National Fire Protection Assoc. Hazard Classification	3-2-2	G9
NPCA HMIS Rating	3-2-2	G10
Electrical Group Classification,IEC-78-8; NEC (US)	T2(300-450°C); Unclassified/Class I, Group D	G
Chemical Oxygen Demand (COD), weight oxygen/wt MAA	1.7	C14
Biological Oxygen Demand (BOD_5), wt oxygen/wt MAA	0.89	G11
pH of Methacrylic Acid in Water *100 ppm Methacrylic Acid* *1000 ppm Methacrylic Acid* *10,000 ppm Methacrylic Acid* *100,000 ppm Methacrylic Acid*	 *3.8* *3.3* *2.7* *2.3*	 *F* *F* *F* *F*

Data Quality: G-Good, Reliable public source; F-Fair, Unverifiable or non-public source; U-Unknown source; C-Calculated by standard methods.

Sources

1 DIPPR
2 OECD/EU Risk Assessment
3 Chemical Properties Handbook-Coefficient of Thermal Expansion of Liquid: Organic Compounds.
4 Knovel Critical Tables – Physical Constants and Thermodynamics of Phase Transitions
5 Heats of Polymerization of Acrylic Acid and Derivatives, Evans and Tyrrall, Journal of Polymer Science, Vol 2, N° 4, 1947
6 Lange's Handbook of Chemistry (15th edition) Table 8.8 pKa Values of Organic Materials in water at 25C
7 Riddick, J.A., Bunger, W.B., "Organic Solvents: Physical Properties and Methods of Purification, 3rd ed.," Wiley Interscience, New York (1970).
8 Weast, R.C., Astle, M.J., "Handbook of Data on Organic Compounds." CRC Press (1985).
9 Building and Fire Code Classification of Hazardous Materials.
10 National Paint & Coatings Association, Hazardous Materials Identification System.
11 Handbook of Environmental Data on Organic Chemicals
12 MOC = LEL x Stoichiometric O_2 moles (4.5 for Methacrylic acid)
13 $SG_{VAP} = MW_{MAA}/MW_{AIR}=86/29$
14 $COD=MW_{O2}$xStoichoimetric$O_2/MW_{MAA}=32x4.5/86$

3 Training and Job Safety

Methacrylic acid is considered to be hazardous under the Occupational Safety and Health Administration's (OSHA's) Hazard Communication Standard (29 CFR 1910.1200) and the EU Classification Packaging and Labeling of Dangerous Substances Directive (67/548/EEC). Therefore, all employees must be provided with adequate health and safety information and training to handle methacrylic acid. The training requirements are listed in the Hazard Communication Standard and the EU Directive.

Before undertaking any training of the employees who are engaged in handling or processing methacrylic acid, the supervisor who will conduct the training must be thoroughly familiar with the storage, handling, and properties of methacrylic acid and with any applicable national, state or local governmental occupational safety and health regulations. Thoroughly review the supplier's MSDS and consult a safety specialist or your supplier before finalizing a safety review of the operations involving methacrylic acid.

4 Instability and Reactivity Hazards

4.1 Polymerization

Methacrylic acid is highly reactive. Polymerization of methacrylic acid can be very violent, evolving considerable heat and pressure and ejecting hot polymer from the site of polymerization.

An explosion hazard exists if the material is in a closed or poorly vented container because pressure build-up can occur very rapidly. Commercially available methacrylic acid is inhibited with methyl ether of hydroquinone (MEHQ), which together with dissolved oxygen prolongs the usable shelf life, i.e., the time before spontaneous polymerization. Commercial grades of methacrylic acid generally have a shelf life of one year at ambient conditions and should be used within that time (see Section 8). Your supplier should be contacted for shelf life detailed information.

Methacrylic acid must never be handled or stored under an inert atmosphere. The presence of oxygen is required for the inhibitor to function effectively. A headspace containing sufficient oxygen should always be maintained above the monomer to ensure inhibitor effectiveness.

There are five main causes of unintended polymerization of methacrylic acid: overheating and photo-initiation, contamination, corrosion, inhibitor depletion, and inhibitor deactivation (via oxygen depletion).

4.1.1 Overheating and Photo-initiation

Commercially available methacrylic acid is inhibited with MEHQ that prolongs the usable shelf life, i.e., the time before spontaneous polymerization. However, this usable shelf life is reduced exponentially with increasing temperature. Therefore, overheating of methacrylic acid must be avoided. Throughout this manual, the recommended safe temperature range for storage of methacrylic acid is 18-40°C. The lower limit (18°C) is intended to provide a reasonable separation from the freezing point (15°C). The upper limit (40°C) is a temperature that testing and experience have shown to be acceptable for storing METHACRYLIC ACID, without degradation of safety or product quality, for periods of time typically occurring in a well-ventilated warehouse anywhere in the world, as long as shelf life is not exceeded. Higher temperatures can be safely tolerated for shorter times such as during transportation or inventory turnover. Never exceed 45°C during a thawing process. Consult your supplier of methacrylic acid to determine if a higher temperature is acceptable. Also, see Section 4.3 Effect of Freezing and Section 6, Thawing of Frozen Methacrylic Acid.
Methacrylic acid can polymerize as a result of photo-initiation. Where sight glasses or other transparent sections are needed for visual observation in methacrylic acid service, they should have covers to exclude light between observations. All containers such as IBC, drums, etc., used for storing methacrylic acid should be kept from the direct UV radiation and should be preferably opaque to direct UV radiation. Store only inside or in a shaded area.

4.1.2 Contamination

Good housekeeping must be exercised to avoid contamination of methacrylic acid monomer. Many compounds are known that promote its polymerization, such as peroxides and compounds which form peroxides and free radicals, including aldehydes, ethers, amines, azides, and nitric acid.

Care must be exercised to avoid contamination of monomer with polymerizing methacrylic acid.
Such polymer «seeds» could be generated in localized or hot stagnant areas, such as dead-headed pumps, and heated transfer lines.

4.1.3 Corrosion

Corrosion in general can also pose a polymerization hazard. Metal ions can initiate polymerization. Metal ions result if there is corrosion in the storage or transportation system. Methacrylic acid will easily corrode iron, carbon steel and similar metals. Refer to 10.2.1 Materials of Construction for proper materials of construction. Corrosion can be caused by using an improper material of construction, accidental introduction of incompatible metals into the system such as leaving a tool in a storage tank, or the contamination of the methacrylic acid with materials such as mineral acids that are corrosive to normal methacrylic acid systems.

4.1.4 Inhibitor Depletion

Inhibitor is depleted with time. Elevated temperatures accelerate depletion. Observe the recommended storage time and temperatures to prevent depletion of the inhibitor as well as premature depletion of oxygen. A special depletion possibility exists during the freezing and thawing of methacrylic acid. See Section 4.3, Effect of Freezing.

4.1.5 Inhibitor Deactivation/Oxygen Depletion

Dissolved oxygen is necessary for MEHQ to function effectively, acting as the initial, and very efficient, radical scavenger. Therefore, methacrylic acid should never be handled under an oxygen-free atmosphere. A nitrogen/oxygen gas mixture containing 5-21% by volume of oxygen at one atmosphere should always be maintained above the monomer to ensure inhibitor effectiveness. Since methacrylic acid vapors in air do not form flammable mixtures at room temperature, air may be used for this purpose.

Oxygen is consumed slowly as part of the free radical scavenging mechanism. Observe the recommended storage time and temperatures to prevent premature depletion of oxygen as well as depletion of the inhibitor. The atmosphere above methacrylic acid in a closed system should be periodically replenished with air or a nitrogen/oxygen gas mixture containing 5-21% by volume of oxygen. Large volumes of liquid should be circulated with at least 5% oxygen present (See Section 9.2.4). Residues in transfer lines and other stagnant areas should be blown out with a nitrogen/oxygen gas mixture containing 5-21% by volume of oxygen, or should be designed to be self-draining.

4.2 Polymerization Detection

Methacrylic acid has the potential to polymerize very rapidly, generating a large amount of heat. A temperature rise that cannot be related to an external heat source should be considered an indication of a runaway polymerization. Observations and sampling of methacrylic acid may be able to indicate the onset of polymerization prior to an observable rise of temperature. The earliest indication of polymerization is the appearance of haze caused by methacrylic acid polymer, which is insoluble in methacrylic acid monomer. There is normally at least one hour after the first observance of haze and the onset of uncontrolled polymerization.

Occasionally on the plant scale, uncontrolled methacrylic acid polymerizations proceed slowly. Therefore, simple temperature rise may indicate an ongoing polymerization. In the case of a slow temperature rise, the presence of visible haze in the monomer should verify whether a polymerization is underway.

> **CAUTION**
>
> Even slow polymerization has the potential to accelerate into a runaway reaction. If the temperature rises above 40°C (104°F) and the rate of rise is greater than 2°C (3.6°F)/hour, and no source of external heat has been identified, this should be considered as the onset of polymerization. If the temperature rises at a rate greater than 5°C (9°F)/hour, the situation is considered critical.

4.3 Effect of Freezing

Freezing of methacrylic acid should be avoided. Thawing of frozen methacrylic acid can be extremely hazardous. Methacrylic acid freezes at 15°C (59°F). As freezing occurs, the first crystals formed contain pure monomer with very little inhibitor; the inhibitor is concentrated in the liquid phase. When freezing occurs in bulk containers, the first crystals, low in inhibitor, will form along the outer wall of the container. The inhibitor will be concentrated at the center. Improper thawing may lead to pools of monomer containing low levels of inhibitor. This condition is made worse by repeated freeze/thaw cycles if the methacrylic acid is not mixed well after each thawing. If possible, the acid should not be thawed by applying heat directly to the outside of the container because the potential of polymerization of the low-inhibited monomer along the walls is possible.

The temperature of the acid should be maintained at 18-40°C (64-104°F). The ideal storage temperature is 20-25°C (68-77°F). Other temperature targets between 18-40°C (64-104°F) may be needed on a seasonal or situational basis.

In the event freezing does occur, follow procedures in Section 6, Thawing of Frozen Methacrylic Acid.

4.4 High Temperature Decomposition

Not all polymerization incidents involve rapid polymerization. Sometimes the reaction proceeds much more slowly. Still, in unvented containers or containers whose vent has plugged (note that small vents can plug easily because of methacrylic acid polymer), high temperatures and pressures can build up over time. If the temperature reaches 195-200°C (383-392°F), methacrylic acid will undergo degradation. It is well documented that methacrylic acid polymer will dehydrate to methacrylic anhydride and water at 200°C (392°F). Some evidence exists that methacrylic acid can undergo decarboxylation at 195°C (383°F) generating carbon dioxide. With either decomposition reaction, very high pressures can be generated in a short period of time in an unvented container. Rupture of the vessel is possible.

> **NOTE:** In the event of an unintended polymerization in an unvented container, high pressures may persist long after the polymerization event is over because of the presence of decomposition gases.

5 Response to Uncontrolled Polymerization

The techniques for responding to an uncontrolled polymerization of methacrylic acid are regularly reviewed for improvements. These will be updated as new information is developed. Use the information below to develop local Emergency Response Procedures. This section alone is not intended to serve as an Emergency Response Procedure by itself.

Approaching any container of methacrylic acid that is thought to be undergoing an uncontrolled polymerization is hazardous because of the possibility of the container's violent rupture. Do not approach a container of uncontrolled polymerizing methacrylic acid without prior emergency planning. Never approach a container of methacrylic acid after it has reached 55°C (131°F) or if the rate of temperature rise has exceeded 2°C (3.6°F)/hour. Consider this for all response choices.

The most effective response to an uncontrolled polymerization of methacrylic acid is the remote addition and mixing of shortstop inhibitor, phenothiazine (PTZ). The final concentration of PTZ in the methacrylic acid to be shortstopped should be in the range of 200 to 1,000 ppm. However, in the case of contamination, restabilization may not be possible at any concentration of PTZ, depending on the nature and concentration of the contaminant. While other choices, mentioned below, may be less expensive, they are also expected to be less effective unless done as extra activity to reduce consequences after shortstop inhibitor, PTZ addition, has already been done.

- Once it has been determined that an uncontrolled polymerization is occurring, (see Section 4.2, Polymerization Detection) establish emergency management control over the area including evacuation if necessary. Safe evacuation distances depend upon many factors including the rate of polymerization, the likelihood of vent pluggage, and equipment design (size, vent area, design pressure, etc.), etc. These should be planned for in advance and be a part of the local Emergency Response Procedures. **Consult your supplier for further advice in the development of your Emergency Response Procedures.**
- If possible, remove insulation from the vessel to allow cooling with fire water. Consider hazards in approaching the tank if the temperature is already above 55°C.
- Apply cooling water to coils, jackets, and to the exterior of the vessel to reduce the temperature of the methacrylic acid. The local emergency response team should be able to set up fire monitors to provide fire water for cooling. Externally applied water may also be effective in knocking down any vapors that may be released.
- If it is determined that it is safe to approach the vessel, the following can be tried to minimize the consequence of the polymerization.
  - Ensure adequate venting area by opening any closed top hatches, especially for tank trucks or rail cars. Caution: Do **not** attempt this if the temperature is already above 55°C or if a local pressure gauge indicates that the vessel is above atmospheric pressure or if the vessel is venting.
  - Add the shortstop inhibitor, PTZ, in a concentrated solution or slurry. Locations storing methacrylic acid should maintain a supply of PTZ for use when needed. MEHQ and HQ are not shortstop inhibitors. MEHQ or HQ can effectively extend the shelf life of methacrylic acid only if there is adequate oxygen in solution. Temperatures significantly above ambient may deplete the oxygen in solution and prevent MEHQ and HQ from working. Temperatures reached during a runaway polymerization will defeat the functionality of MEHQ or HQ. MEHQ or HQ will not have a significant impact if added to a runaway polymerization of methacrylic acid.

- Diluting the methacrylic acid with water may reduce the consequence of the polymerization if the temperature of addition is low enough, below 55°C (131°F). This should be done only if there is sufficient space left in the container to increase the volume by at least 30% with water addition and also allow mixing.
  Adding inadequate dilution water or inadequately mixing the dilution water with the reacting methacrylic acid or adding at a temperature that could allow the mixture to reach 100°C could increase consequences (increased venting because water is more volatile than methacrylic acid, increased probability of plugging the vent with a rise in the level of the liquid, and increased probability of breaching the vessel if reaction does not stop). Remember that shortstop inhibitor, PTZ, is not soluble in water. Addition of shortstop inhibitor, PTZ, and mixing should be done prior to any water addition.
- If impact to the environment and to personnel exposures is acceptable, consider discharging the contents of the container into a diked/bunded area.
- Consider moving a mobile container away from people and equipment; barricading of drums or totes/IBC is another option.

CAUTION

Do not attempt to mix the contents of the container unless either shortstop inhibitor or dilution water has been added to the methacrylic acid.

A vessel undergoing an uncontrolled polymerization may experience high enough temperature to cause venting.
Note: A polymerizing vessel that stops venting may have a plugged vent. The potential for a violent vessel rupture may exist for many hours. Do not approach a vessel that has ceased venting until remote temperature sensing indicates that the vessel contents have returned to the ambient temperature.

6 Thawing of Frozen Methacrylic Acid

Methacrylic acid freezes at 15°C (59°F). Improper thawing of frozen methacrylic acid can be extremely hazardous. See Section 4.3, Effect of Freezing.

6.1 Thawing of Frozen Drums / IBC's / Totes

The thawing of frozen methacrylic acid in drums or other small containers can best be accomplished by placing the drums in a heated room at temperatures up to 40°C (104°F). This will allow the acid to melt slowly within a 48-hour period. Monitor the temperature of the room closely to prevent overheating. Drums should be rolled or rotated every 6-8 hours during thawing to mix the contents. IBC's/Totes should be placed on a shaker plate during thawing to mix the freshly thawed material and to speed up the thawing process. After thawing, methacrylic acid should be stored between 18-40°C (64-104°F), ideally 20-25°C (68-77°F).

- Never store adjacent to heat sources.
- Never withdraw material from a partially frozen or partially thawed container of methacrylic acid. Such material may have low inhibitor levels or it may contain most of the inhibitor required for the entire contents of the container.
- Never apply electric heating bands to thaw containers as these generate high surface temperatures.
- Never apply steam to the outside of the container.

6.2 Thawing of Frozen Bulk Containers

CAUTION

Do not attempt to thaw a frozen bulk container of methacrylic acid unless you have received prior approval from your supplier. Specific training may be required.

If you can anticipate receipt of frozen containers of methacrylic acid, develop a thorough procedure for safe thawing in advance of the first receipt. Contact your supplier for advice on design and operations with regard to possible receipt of frozen methacrylic acid containers.

Bulk containers can be safely thawed through the use of tempered water systems. The temperature of the water should never exceed 45°C (113°F). Use only automatic temperature controlled, "Fail Safe" alarmed, tempered water systems. The temperature of both the circulating water and the thawed portion of the monomer should be closely monitored. If possible, the monomer should be well mixed to ensure that dissolved oxygen and the inhibitor is well distributed during thawing as well as to enhance heat transfer.

As soon as the methacrylic acid is thawed, maintain the temperature of the thawed methacrylic acid at 18-40°C (64-104°F) and empty the container into the methacrylic acid storage tank.

CAUTION

Never use live steam. Localized hot spots must be avoided.
Never use steam-water mixing nozzles or tees directly in heating coils, jackets, etc., for thawing.
An increase in steam pressure or loss of water supply would create immediate high temperature conditions resulting in a polymerization.
Never remove any material from a partially frozen container. If possible contents should be thoroughly mixed during and after the thaw cycle to ensure uniform mixing of the inhibitor before any liquid is withdrawn.
If possible, mix by re-circulation, agitation, or by means of an eductor. Totally thawed methacrylic acid can be pumped in its entirety to a storage tank for completion of mixing.
If frozen methacrylic acid is discovered in a vessel after emptying, return warm methacrylic acid to the vessel to provide inhibitor and a heat transfer source for thawing.

NOTE: If you are surprised by a frozen container of methacrylic acid or cannot safely thaw the methacrylic acid in accordance with these guidelines, please contact your supplier immediately.

6.3 Thawing Plant Equipment

A concise procedure for the safe thawing of a normal storage tank cannot be given. It depends upon the precise details of the equipment and the circumstances. Contact your supplier for advice.

Bulk containers can be safely thawed through the use of tempered water systems. The temperature of the water should not exceed 45°C (113°F). Use only automatic temperature controlled “Fail Safe” alarmed, tempered water systems.
The temperature of both the circulating water and the thawed portion of the monomer should be closely monitored. The monomer should be well mixed to ensure that the inhibitor is well distributed and oxygen gets redissolved into the liquid.

As soon as the material is thawed, maintain the temperature of the thawed methacrylic acid at 18-40°C (64-104°F), and preferably between 20-25°C (68-77°F).

CAUTION

Never use live steam or electrical heating systems such as electrical tape systems or mantles.
These may cause localized hot spots.
Never use steam-water mixing nozzles or tees directly in heating coils, jackets, etc., for thawing. An increase in steam pressure or loss of water supply would create immediate high temperature conditions.
Never remove any material from a partially frozen tank. Tank contents should be thoroughly mixed during and after the thaw cycle to ensure uniform mixing of the inhibitor before any liquid is withdrawn.
Mix by re-circulation, agitation, or by means of an eductor.

7 Health Concerns

7.1 Toxicity

The principal hazard of methacrylic acid is its corrosivity to tissue and mucous membranes. Direct skin contact causes severe burns if the acid is not immediately and thoroughly removed. Inflammatory symptoms and blister formation can appear as late as 24 hours after exposure. However, tissue destruction occurs within the first few minutes. Healing from such injuries is occasionally delayed. See Section 7.2.3, Contact with Skin for more information.

The cornea and mucous tissues of the eye region may be severely damaged by contact with methacrylic acid. If not flushed immediately and thoroughly with water, permanent damage may result. See Section 7.2.1, Contact with the Eyes for more information.

Although ingestion is not a typical route of exposure to chemicals in the industrial environment, if methacrylic acid is swallowed it severely damages the mucous membranes of the mouth, throat, esophagus, and stomach. See Section 7.2.4, Ingestion for more information.

Inhalation of high concentrations of methacrylic acid vapors or mists causes burns of the respiratory tract and the possibility of delayed formation of pulmonary edema. Inhalation of lower concentrations produces strong nasal irritation accompanied by lachrymation. No serious adverse health effects have been reported following single or repeated exposures to airborne concentrations of 10-20 ppm. See Section 7.2.2, Inhalation for more information.

Your supplier's current MSDS should be consulted for current toxicological information.

7.2 First Aid

In order to minimize adverse consequences of methacrylic acid incidents, all personnel assigned to work with methacrylic acid must be aware that prompt and appropriate response is essential. First aid must be administered immediately.
One prerequisite for the proper management of incidents is the installation of a sufficient number of conveniently located emergency safety showers and a periodic testing program to ensure they are operative when needed.

All injured personnel should be referred to a physician who should be given a detailed account of the incident. Consideration should be given to supplying the physician or hospital emergency room, where medical help will be sought, with a copy of the supplier's MSDS. Medical management aspects of that document should be reviewed with the physician.

7.2.1 Contact with the Eyes

If even minute quantities of methacrylic acid enter the eyes, the eyes should be irrigated immediately and thoroughly with water for a minimum of 15 minutes. The eyelids should be held open and away from the eyeball during the irrigation to ensure contact of water with all the tissues on the surface of the eye and lids.
The eye irrigation should be continued for a second period of 15 minutes if the odor of methacrylic acid persists. Obtain a Physician's assistance (preferably an eye specialist) or that of another trained emergency health professional as soon as possible and transport to a suitable clinic or hospital. No oils or oily ointments or neutralizers should be put in the eyes or on the eyelids unless prescribed by the physician.

7.2.2 Inhalation

Personnel affected by methacrylic acid vapors must be moved at once to an uncontaminated atmosphere. If an individual is not breathing, administer artificial respiration. Obtain a physician's assistance or that of another trained emergency health professional as soon as possible and transport to a suitable clinic or hospital. If breathing is difficult, trained personnel should administer oxygen.

7.2.3 Contact with Skin

The emergency safety shower should be used immediately to remove methacrylic acid. Once under the safety shower, immediately remove all clothing and shoes. Wash with large quantities of water. Continue washing for at least 15 minutes until odor has disappeared. Washing with soap may help remove residual methacrylic acid from the skin and reduce the severity of the injury. After showering, get immediate medical attention. No salves or ointments should be applied to chemical burns for at least 24 hours unless prescribed by a physician.

All contaminated clothing should be properly decontaminated before reuse. Where decontamination is not feasible, clothing should be disposed of properly. Contaminated shoes and other leather items cannot be decontaminated and should be discarded. Under no circumstances should contaminated clothing be taken home for laundering.

7.2.4 Ingestion

Although ingestion of chemicals is rare in the industrial setting, in the event of methacrylic acid ingestion the affected individual should be made to drink large quantities of water. Do not induce vomiting. Consult a physician.

7.3 Industrial Hygiene

Exposure to methacrylic acid by inhalation, ingestion, or skin or eye contact should be prevented by a combination of engineering controls and prudent work practices. Engineering controls such as closed systems and local exhaust ventilation should be the primary emphasis and must be in compliance with national, state and local governmental regulations. Personal protective equipment (PPE) must be used.

Occupational health standards-setting organizations have established workplace exposure limits expressed as parts of methacrylic acid per million parts of air (ppm). Examples of such organizations include: the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) in the U.S., the Health and Safety Executive (HSE) in the U.K., and the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK) in Germany. In the past, these values have generally been 20 parts of methacrylic acid per million parts of air (ppm). Therefore, the reader is advised to refer to up-to-date publications for the current values. These workplace exposure limits are time-weighted average values, which means that exposures in excess of 20 ppm are permitted providing that there are offsetting periods below 20 ppm such that the overall exposure averages 20 ppm or less for the 8-hour work day. In addition, some official standards include a "Skin" notation, indicating that methacrylic acid can be absorbed in harmful amounts through intact skin. Please refer to your relevant national or governmental authority for the current exposure standard information.

7.4 Personal Protective Equipment Guidelines

Personal protective equipment (PPE) is not an adequate substitute for engineering controls, safe work practices, and intelligent conduct on the part of employees working with methacrylic acid. It is, however, in some instances the only practicable means of protecting personnel, particularly in emergency situations.

Use the guidelines below as a starting point for developing your own Personal Protective Equipment procedures. The hazard of each task must be thoroughly assessed, appropriate personal protective equipment must be selected, and training in the correct use and care of the PPE must be provided.

Testing has shown that butyl rubber gloves and fluoroelastomer gloves provide superior resistance to permeation by methacrylic acid. Consult a methacrylic acid supplier for the most current information on glove materials.

7.4.1 All Personnel

All personnel who are in the general area where methacrylic acid is being handled should wear the appropriate personal protective equipment. This protective equipment should be worn even if an individual is not planning to come in contact with the methacrylic acid processing equipment.

7.4.2 Routine Work

Personnel engaged in routine work with a small risk of limited exposure, such as collecting a sample or operating processing equipment, should wear the following protective equipment: chemical-resistant gloves, hard hat, safety shoes, and chemical splash goggles. Depending on the situation, consider wearing chemical-resistant boots if walking surface contamination is anticipated and a face shield if methacrylic acid spray or mist is anticipated. In addition, air-purifying respiratory protective equipment should be worn if air monitoring has demonstrated that airborne concentrations of methacrylic acid are above the established exposure limit and below 200 ppm.

7.4.3 Non-Routine Work

Personnel engaged in non-routine work and/or work with moderate risk of exposure such as unloading tank trucks and rail cars, opening vessels, breaking lines, or cleaning minor spills and leaks, should wear the following personal protective equipment: acid suit, chemical-resistant boots and gloves, hard hat, and chemical splash goggles. Wear a face shield in the case of opening drums or lines that may be under pressure or an acid hood with an acid suit if there is a more serious splash potential. Air-purifying respiratory protective equipment may be worn if airborne concentrations of methacrylic acid are between 20 and 200 ppm. If greater than 200 ppm, a supplied-air respirator is required.

7.4.4 Emergencies

Any time there is a risk of exposure to airborne concentrations of methacrylic acid in excess of 200 ppm or to unknown airborne concentrations, full protective gear must be worn. In such events as major spills, vapor clouds or fire situations, wear full protective gear: a supplied air respirator in positive pressure mode, hooded acid suit, chemical-resistant boots, hard hat, and chemical splash goggles.

In the event of a release of methacrylic acid, the area should be evacuated immediately and should be entered only by properly trained personnel equipped with appropriate PPE. It is advisable to have several sets of PPE available at all times. This equipment should be stored outside of, but near, the area where the methacrylic acid is used.

8 Fire and Explosion Hazard

Methacrylic acid has a moderate flash point and low vapor pressure at typical handling temperatures. Ignition may occur, however, if excessive amounts of mist or aerosol have formed in the air. Ignition sources can be spark discharges from static electricity or any other source.

If a fire should occur, water can be used effectively since methacrylic acid and water are miscible in all proportions at temperatures above the freezing point of methacrylic acid or methacrylic acid/water mixtures: >15°C (59°F). Fire fighters should be informed about the water-miscible nature of methacrylic acid.

During transfer between containers, the containers must be electrically interconnected (bonded) and properly grounded/earthed. Splash filling into a tank should be avoided unless velocity is low enough to prevent static electricity build up. This can be achieved by using a dip tube. If mixing nozzles are used in storage tanks, the minimum storage volume should be chosen such that the liquid surface is 500 mm (20 inches) above the nozzle outlet at all times in order to avoid spraying.

In the event of major incidents involving large spills or fires in storage tanks or rail cars, an assessment of all pertinent facts is critical to the safe management of the situation. Factors to consider are the probability of a vapor cloud and its dispersion, explosion, corrosivity, and the effect of the fire and heat on surrounding objects or materials. Some situations in the past have been best managed by allowing a fire to burn out.

In case of fire, evacuate non-essential personnel to a safe location. Carbon dioxide or dry chemical extinguishers may be used on small fires. In addition to water, large fires may also be fought with «alcohol» or universal-type foam, water fog, carbon dioxide, or dry chemical methods. Consider permanent installation of fire monitors to enable the continuous application of fire fighting water to storage areas without personnel exposure. Containment of runoff of fire fighting materials should be planned as required by regional, country, state or local authorities. See Section 7.4.4, Emergencies, for PPE to be worn for all emergencies, including fire.

8.1 Special Hazards

Any drums or containers exposed to fire should be kept cool with water spray while personnel are fighting the fire. Fire fighting personnel should operate from a remote location if possible. In a fire, sealed containers may rupture explosively due to polymerization and autoignition of the vapors may occur.

The above information should be used to develop a Fire Emergency Response Plan.

9 Storage and Handling

Please read this entire Manual before storing methacrylic acid or before designing a storage system for methacrylic acid. All preventive measures described in this Manual must be followed to minimize the possibility of an uncontrolled polymerization that may proceed with violence under certain conditions. See Section 4, Instability and Reactivity Hazards, for a description of the polymerization hazards.

9.1 Drum/IBC/Tote Storage

Methacrylic acid is commonly sold in either steel drums with a polyethylene liner or high molecular weight, high-density polyethylene drums. In some regions of the world, reusable stainless steel drums may be used. IBC/totes of various constructions (including Ultraviolet radiation protection and preferably a grounding option) may also be used and should be treated similarly to drums.

- The drums/IBC/Totes must be stored according to applicable national, state and local regulations. Lacking other guidance or limits, drums should be stored not more than 2 high and a path of 1.5 meters (5 feet) should be kept free around each block, to provide ventilation and both normal and emergency response access.
- Indoor storage is recommended. Warehouses must be well ventilated. The temperature of the warehouse should be between 18-40°C (64-104°F) and preferably <30°C (<86°F).
- If drums/IBC/Totes are stored externally, they should be protected from direct sunlight.
- If drums/IBC/Totes freeze, follow thawing procedures described in Section 6.1, Thawing of Frozen Drums/IBC's/Totes.

9.1.1 Drum/IBC/Tote Handling

It is preferable that drums/IBC/Tote be transported in a manner so as to ensure the temperature stays between 18-40°C (64-104°F). When a load of drums/IBC/Totes is received, open the doors carefully before entering. If a strong odor is present, indicating a leaking container, immediately call the supplier. See Section 11.2, Spill and Leak Control.

9.1.2 Drum/IBC/Tote Emptying

To empty a drum/tote/IBC in an area where flammable atmosphere may occur (e.g. Zone 2 rating) the following procedures must be followed:

- Before drums/IBC/Totes are opened, they should be supported and grounded/earthed.
- Drums/IBC/Totes and fittings should never be struck with tools or other hard objects that may cause sparking or puncture.

NOTE: Drum contents may be under pressure or vacuum.

When removing plugs (bungs) from a drum of methacrylic acid (or opening an IBC/Tote), the operator should wear PPE recommended in Section 7.4, Personal Protective Equipment Guidelines, and should use a bung or plug wrench. The operator should place the drum bung up, and loosen the bung. Note that the drum/IBC/Tote contents may be under pressure or vacuum. After the plug starts to loosen, it should be given not more than one full turn. If internal pressure exists, it should be allowed to escape to the atmosphere. Only then should the operator loosen the plug further and remove it.

The preferable safe method for emptying drums/IBC/Totes is by pump or by gravity. Note that electric pumps must comply with the area electrical classification. When emptying by gravity, use self-closing valves. Vent drum/IBC/Tote while emptying. Do not use pressure to empty drums.

Do not cut, drill, grind, or weld on or near drums/IBC/Totes. The heat from such work could ignite residual material in the drum/IBC/Tote. Residual vapors may explode on ignition.

Improper disposal or reuse of containers may be dangerous and/or illegal.

9.1.3 Drum/IBC/Tote Disposal

Empty drums/IBC/Totes are hazardous because of residual liquid and vapor. Dispose of drums/IBC/Totes in accordance with applicable regional, national, state, and local requirements. Before a drum/IBC/Tote is scrapped, it should be repeatedly washed with water to remove traces of methacrylic acid and then rendered unusable by crushing or piercing. Dispose of rinse water properly. See Section 11.1, Waste Disposal.

9.2 Bulk Storage

Methacrylic acid must be stored under an atmosphere containing 5-21% oxygen. Methacrylic acid suppliers can provide information on special design features required to cope with specific hazards of bulk storage. Consider consequences/risk when planning an installation. Larger bulk quantities of the acid imply higher risk because of higher potential consequences. All efforts should be made for control and surveillance of the storage temperature within the prescribed limits of 18-40°C (64-104°F), and preferably <30°C (<89°F). Redundant control devices are strongly recommended.

Conduct a hazard review and/or risk analysis of the storage facility to ensure adequate safeguards are in place to reduce the risk of polymerization and exposure. Design the storage tank to maintain temperature within 18-40°C (64-104°F), and preferably <30°C (<89°F).

Bulk storage tanks may be positioned inside a heated building. This provides independence from weather conditions, thus reducing costs.

A typical installation for an outdoor tank is shown in the Appendix to this manual. The special features of the design are derived from long-term experience and have proven to be reliable.

For environmental reasons, tanks and pumps should always be positioned in a diked/bunded area. Structures made of concrete are attacked by methacrylic acid. Suitable coatings should be applied in order to prevent attack of the concrete. All applicable regional, national, state and local governmental regulations must be observed.

9.2.1 Materials of Construction

Preferred construction materials for tank, pump and pipe installations are stainless steels, e.g., EN 58 C or H; DIN 1.4571 or 1.4541; US 316L or 321. Aluminum alloys can be used for anhydrous methacrylic acid. Polyethylene, polypropylene, EPDM, or fluoropolymers are also suitable as materials of construction for methacrylic acid and may be useful for accessory equipment such as gaskets and valve parts. Carbon steel and other heavy metals must not be used due to the corrosive nature of methacrylic acid. Metals may also cause initiation of polymerization. All applicable regional, national, state and local governmental regulations must be observed.

9.2.2 Pressure Relief

There is no guaranteed or warranted method for relieving the pressure from a methacrylic acid runaway reaction and the consequent potential of violent rupture of the container. Therefore, low design pressure (API atmospheric) tanks are recommended. Although no detailed experience with runaway reactions in full size tanks is available, weak seam or frangible roof designs are believed to provide the best protection from a failure. Roof guide cables should be considered to control the trajectory of such a roof. In addition, oversized rupture disks or weight-loaded lids ("weighted manway cover") may be acceptable.

For the natural breathing of the tank, a conservation valve should always be installed. Various designs such as weight-loaded pressure pallet valves or breathing valves with flexible diaphragms are commercially available. Seal pots with glycol can be used instead of conservation vents if they are properly designed and maintained. They may also serve as an overflow device.

Uninhibited methacrylic acid vapor can condense or crystallize on cold surfaces, such as relief valve inlets or rupture disks. The uninhibited condensate may then polymerize. Pressure relief devices and their connected lines should be checked periodically for the presence of polymer and/or frozen methacrylic acid, to prevent interference with their proper operation. Relief valves and nozzles can be electrically traced and insulated to help control polymer formation. They can continue to be flushed continuously with dry air.

Environmental protection alternatives, such as containment of vapors with closed loop unloading or venting through a scrubber or incinerator, may also be considered.

9.2.3 Temperature Control

Because methacrylic acid freezes at 15°C (59°F), it is essential that reliable temperature control be installed on outdoor tanks in climates with temperatures expected below methacrylic acids' freezing point.

Insulate all tank surfaces, nozzles, manways and piping. All insulating structures should be covered with a protective shell to keep rainwater from penetrating into the insulation material. Humidity enhances heat loss and could therefore cause uncontrolled cooling of the stored material. Protruding surfaces should be entirely incorporated into the insulation mantle to prevent condensation or crystallization of acid vapors, which might result in polymerization.

Control of heat loss may not adequately protect methacrylic acid from freezing. Additional heating devices are needed to balance the energy loss and to keep the tank at the required temperature for storage. Either an internal heating coil or an external heat exhanger is suitable. The heat exchange surface must be generously designed for high-energy losses during unusually cold weather conditions.

The design of heating devices must include control instruments that are suitable to reliably prevent overheating the acid. One such system is a double-circuit warm water system with steam or hot water in the primary and a glycol-water mix in the secondary circuit. A heat exchanger is commonly used to achieve the transfer between the circuits. Provision must be made to automatically control and alarm the temperature in the secondary circuit at preset high and low points. Maximum permissible temperature in the secondary circuit is 45° C (113°F), minimum temperature should be set at 18°C (64°F). Under no circumstances should live steam come in contact with methacrylic acid. The primary circuit must shut off automatically if instruments fail and the preset high temperature is reached.
Transfer lines to and from the tank are particularly vulnerable to freezing in cold climates. All outdoor lines should be traced with warm water or self-limiting electrical heat tracing. The design of the heating system should be capable of meeting all potential heat losses. Only electrical heat tracing with self-limiting properties should be used and only then if it can be ensured that overheating of the material cannot occur.

The most reliable way to detect a runaway reaction is by continuously monitoring the temperature of the inventory. The temperature monitoring system must have redundancy and be capable of determining the absolute temperature of the bulk liquid as well as the rate of temperature rise. Recording the temperature is helpful, and the use of high temperature alarms is strongly recommended.

At least two independent thermosensors (thermocouples) should be installed near the bottom of the tank so that they are always covered by the monomer level. In larger tanks it is sometimes advantageous to have a second pair of sensors installed above the lower third of the total tank height. It is of the utmost importance that the thermosensors stop the primary heating circuit in the event that the preset high temperature point has been exceeded.

9.2.4 Pumps and Transfer Lines

It may be appropriate to locate pumps in a heated building or in heated cabinets. Care must be taken to ensure that pumps are never positioned close to a heat source such as radiators or steam pipes. In the event of polymerization, polymer adhering to pump rotors can exert centrifugal forces strong enough to shatter operating pumps.

Centrifugal chemical pumps or seal-less pumps, such as magnetic or canned motor pumps with external cooling, are appropriate for transfer services for methacrylic acid. Centrifugal pumps, either packed or with a gliding disk seal, may require more maintenance due to the poor lubrication properties of methacrylic acid. Canned motor pumps and magnetic coupled pumps have excellent performance properties with respect to leaks, but are sensitive to dry operation that usually leads to total loss of the pump. Therefore, a low/no flow switch should always be installed to protect pumps from dry operation or dead heading.

Care must be exercised to avoid deadheading of pumps since this might overheat the monomer. A temperature sensor or a flow control device combined with a motor switch should be installed on the pump discharge side and before the shutoff valve, preferably in the pump housing. For magnetic drive or canned pumps, a temp sensor must be installed within the pump body. Centrifugal pumps present the potential for dangerous splashes if methacrylic acid leaks through pump seals or glands. Therefore, pump seals/glands, flanged fittings, and valve stems should always be provided with splash collars.

Consideration should be given to unloading and re-circulating the material with the same pump. For this purpose the circulation loop should be routed into a dip pipe running through the tank roof reaching to the very bottom of the tank. An anti-syphon device such as a hole in the dip tube in the vapor space should be installed. The use of non-return (check) valves is not recommended in this application as they may plug. The circulation loop should be arranged so that methacrylic acid will always drain towards the storage tank in the event of an interruption in circulation or transfer.

The oxygen content of the inventory must be maintained to keep the inhibitor working. An air atmosphere is acceptable. In the event that less than 21% oxygen is desired in the vapor space, oxygen level must be reliably kept above 5%. Re-circulation of the contents on a regular basis, at least every 4-6 weeks will keep adequate oxygen dissolved in the liquid. Air is recommended for any purges that enter the tank such as level devices or pressure detection devices. In no event should inert gas such as nitrogen be allowed to completely purge the vapor space. [Reference Section 4.1.5].
Provision for draining lines is helpful in order to avoid stagnant material in case of an extended shutdown. The drainage valve(s) should be installed at the lowest point(s) of the pipe system. The drainage branch should be close coupled so as to not form a dead leg that can contain stagnant material.

To limit vapor emissions during monomer transfers, it is advisable to use a vapor return line to allow the exchange of acid vapor between the headspace of the storage tank and the shipping container. The vapor return line (back-venting pipe) in a closed loop unloading system should be designed with a slight inclination toward the storage tank so that condensed liquid can drain back into the tank. The vapor return line should be equipped with a shut off valve on the end connected to the transport vessel. Some locations may also require a flame arrestor on the end close to the tank. Insulation and tracing for such systems should be considered in cooler climates.

10 Shipping

10.1 General

When shipped in tank trucks or rail cars, methacrylic acid is transported in insulated containers, in compliance with ADR/RID/GGV/GGVE Class 8 Packing Group III specifications in Europe and as methacrylic acid, stabilized, 8, UN2531, PGII under US DOT regulations.

Tank trucks may or may not be heated. They should be fitted with at least one temperature gauge. Heat exchanger tank trucks are equipped with a special heating system to prevent the methacrylic acid from freezing. Temperatures greater than 40°C can be hazardous and should be immediately investigated. The captive glycol-water system is heated by the tractor's radiator water by means of a separate trailer mounted exchanger. Proper design of such a heat exchanger will only compensate for heat loss, to avoid overheating. The temperature of the captive glycol-water mixture should not exceed 45°C. Direct heating of the methacrylic acid with tractor radiator water is hazardous because it is too hot.

If the temperature has fallen below 20°C (68°F), or if as a result of some unforeseen event the truck cannot safely proceed to its destination in time, all efforts should be made to park the truck in a heated garage or carriers' heating station. The driver must inform the supplier as soon as possible.

Under no circumstances must a container of methacrylic acid be connected to a hot water supply or electrical heating without consent of the supplier.

CAUTION
Live steam must never be applied to containers to heat or thaw frozen methacrylic acid.

10.2 Unloading Sites

Tank truck unloading facilities should be level, constructed of concrete or other impervious material, and in a location where it can be easily and safely maneuvered. As methacrylic acid attacks concrete, an acid-resistant concrete coating is recommended. The drainage arrangements should be away from the truck and exposed structures, and suitable for the collection of spills for recovery or appropriate disposal. Where access to the top of the container is required, the site should be equipped with stairs and a platform or consider a fall arresting restraint cable system. An electrical grounding cable is required and must be attached to the transport vessel prior to unloading.

10.3 Procedures for Unloading Tank Trucks

Prior to entering the unloading area, the tank truck should be visually inspected for leaks and other irregularities.

Prior to unloading, the following should be confirmed:

- The engine has been stopped.
- The truck brakes have been applied and the wheels are blocked.
- The tank is connected to the grounding/earthing cable.
- Personnel are wearing the correct PPE.
- Compare the trailer number with that on the bill of lading.
- The tank truck contents have been positively identified as methacrylic acid.
- All connections have been made and are correct.
- Check and record the temperature of the contents. Consult the supplier if the temperature is not within the range of 18-40°C (64-104°F).
- Verify that the receiving vessel will hold the entire contents of the tank truck or iso container.

Emergency showers and eye wash facilities must be available at unloading sites. During the unloading process, the area should be chained off and posted with signs warning others to stay away from the area. The driver must stay close to the vehicle during the unloading process, but not in the cab. The unloading should be continuously monitored until completed.

During cold weather the acid may be frozen, particularly in the valve area. A safe procedure for thawing the outlets is by winding cloth or other absorbent material around the line and then splashing it with warm water of 45°C (113°F).
The procedure may have to be repeated several times until the plug has been completely thawed. Live steam must never be used to thaw unloading equipment.

Before transfer lines and vapor return lines are connected to the container, the contents of the tank truck must be positively identified as methacrylic acid. If a sample for testing or a retain sample is required, the operating personnel wearing the correct PPE should open the lid, first taking care to ensure that any accumulated overpressure is vented, and withdraw an appropriate amount of material.

Transfer of methacrylic acid should always be performed by pump. In several countries the use of compressed air for the transfer of flammable or combustible liquids is explicitly prohibited. In addition, the use of compressed air is extremely hazardous with respect to spills and splashes if the transfer hose should break or leak because the leak can continue until all the pressure drains from the leak. Under no circumstances may inert gases be used to transfer methacrylic acid because of the danger of spontaneous polymerization. In instances where compressed gas has been used to blow lines empty, a pressurized gas mixture of nitrogen with a maximum of 21% oxygen and a minimum of 5% oxygen has been used. A mixed gas system can be simple or complex, depending on the application and desired safeguards. A simple system employs regulators on the nitrogen and air sources. More sophisticated air-nitrogen mixing systems use oxygen sensors and flow controllers. The oxygen analyzer can feed into the flow controller and/or an emergency shutdown system. During system design, careful consideration must be given to the instrumentation failure modes.

If a spill or overflow should occur during an unloading operation, the pump should be turned off, valves closed, and the spill cleaned up before any other action is taken.
The unloading procedures should follow the following sequence:

1 Connect the vapor hose and open the valves to equalize pressure. A qualified person assigned for this duty should carefully check the transfer connections for proper alignment and to confirm that the storage tank is correct.
2 Remove the protection cap of the coupling. The protective caps on discharge pipes must be unscrewed with particular care because the pipes may be filled with acid if the bottom valve of the container is leaking.
3 Connect the liquid line and open the external valve.
4 Open the internal valve.

5 Start the pump. Once the flow has started, continue to monitor the vapor return line gauge to confirm the flow and to avoid pulling a vacuum that may implode the vessel.
6 When the vessel is empty, shut off the pump and close all liquid and vapor valves.
7 Drain and disconnect the hoses and replace the caps.
8 Leave the labels in place (according to the ADR/RID or IMDG or national guidelines).
9 Disconnect the earthing cables and remove the wheel chocks.
10 Verify that the vessel is empty. If the vessel cannot be emptied for whatever reason, contact immediately your supplier.

10.4 Procedures for Unloading Rail Cars

Written unloading procedures are required for safe operation and may be required by law.

In addition to the requirements for unloading tank trucks enumerated above in Section 10.3, in advance of unloading the rail car the following should be completed:

- Compare the car number with that on the invoice.
- Check and record the temperature of the contents if possible. Consult supplier if the temperature is not within the range of 18-40°C (64-104°F).
- Ensure that the train crew has accurately spotted the rail car at the unloading line.
- Secure the unloading track from rail access during unloading. At each accessible end of the car being unloaded, place derails approximately one car length away or else close and lock a gate or switch.
- Place a caution sign on the track or car warning persons approaching the car from the open end or ends of the siding. Leave the sign in place until after the car is unloaded and disconnected from the discharge connection.
- Verify that the receiving vessel will hold the entire contents of the rail car.

The unloading procedures should follow the following sequence:

1 Connect the vapor hose and open the valves to equalize pressure.
2 Remove the protection cap of the coupling.
3 Connect the liquid line and open the external valve.
4 Open the internal valve.
5 Start the pump. Once the flow has started, continue to monitor the vapor return line gauge to confirm the flow and to avoid pulling a vacuum that may implode the rail car.
6 When the rail car is empty, shut off the pump and close all liquid and vapor valves.
7 Drain and disconnect the hoses and replace the caps.
8 Leave the labels in place (according to the ADR/RID or IMDG or national guidelines).
9 Disconnect the earthing cables and remove the wheel chocks.
10 Verify that the vessel is empty. If the vessel cannot be emptied for whatever reason, contact immediately your supplier.

10.5 Transportation Incidents

In the event of a spill, fire, or suspected polymerization, immediately contact the appropriate local or national transportation emergency clearing organization. This would be, for instance, TUIS in Germany, CANTREC in Canada or CHEMTREC in the US.

If a shipment in a railcar, tank truck, drum, intermediate bulk container [IBC/ tote] becomes damaged so that delivery cannot be made safely, every effort should be made to move the container away from people and property. Police and fire departments are to be notified and the public is to be restricted from the area.

10.6 Personnel Protective Equipment with Bulk Containers

A chemical resistant splash suit, gloves, boots, eye protection, and respiratory protection should be considered necessary when loading and unloading bulk containers. Safety glasses with chemical splash goggles and face shields are considered full eye protection. In the absence of a proper risk assessment, full protective PPE equipment should be required when sampling or making and breaking any connections.

10.7 Thawing Shipping Containers

Thawing of shipping containers can be extremely dangerous if proper procedures are not followed. See Section 6 for details. Methacrylic acid containers can be thawed safely with moderate heating and not steam. Bulk containers may be warmed in heated garages. Bulk containers with circulation systems can be thawed with tempered water through heating coils. Drums may be thawed by placing them in heated rooms at temperatures between 20°C and 40°C and then mixed by rolling the drum on the floor, on a drum roller or pallet wrap. Never use direct steam or electrical heating wrappers on drums or totes. Mixing is necessary to distribute the inhibitor and dissolved oxygen. Never remove acid from a partially thawed container.

11 Environmental Considerations

National, state and local governmental regulations governing waste disposal require that producers and users of chemical products be fully aware of viable alternatives for the safe disposal of waste materials and to select and practice a disposal method or process that assures compliance with all applicable requirements. The treatment or disposal of methacrylic acid as a specific chemical can be determined by comparing the physical and chemical properties with regulatory standards.

Discharges into navigable waters, public or private sewers, or air, disposal in landfills, and by incineration, are all controlled by governmental (local, regional, national, and international) laws and regulations. Noncompliance is subject to criminal or civil penalties, or both.

11.1 Waste Disposal

Local, regional, national, and international regulations governing waste disposal make it essential for producers, suppliers, haulers, and users of monomers to be fully aware of viable options for the disposal of materials containing methacrylic acid. Materials to be disposed of include residues from production and cleaning operations as well as waste material from spills.

Minor spills of the methacrylic acid may be washed into a biological treatment plant after notifying local treatment facilities. Diluted methacrylic acid biodegrades readily in the environment. However, methacrylic acid may be toxic to the system if the bacteria have not been properly conditioned to it. Accordingly, the initial feed rate should be low with a stepwise increase if a significant amount is to be fed into the treatment unit. The maximum concentration should not exceed 1000 mg per liter.

Solid material containing methacrylic acid, such as absorbents or polymeric material, can be disposed of by incineration. Disposal in landfills must be thoroughly reviewed with authorities and should be practiced only as a last choice.

For disposal of laboratory wastes or retained samples, great care must be exercised to keep methacrylic acid separate from incompatible materials, such as peroxides, which may initiate polymerization.

11.2 Spill and Leak Control

Emphasis should be placed on the prevention of leaks and spills through careful design and good operating procedures. Written spill and leak response procedures are recommended and may be required by law. Do not allow spills to enter drains, sewers or watercourses. Notify your appropriate regulatory body if spills or uncontrolled discharges enter watercourses.

Methacrylic acid is not likely to persist in surface waters over an extended period of time. All efforts must be made to prevent spills from running into public surface waters. In the event of accidental spillage of methacrylic acid into surface water or to a municipal sewer system, the responsible pollution control agencies must be promptly notified.

If there is a facility capable of treating methacrylic acid, small spills may be washed to the chemical waste treatment sewer with large amounts of water. Small spills of up to 5 liters can be suitably absorbed in commercially available spill cleanup kits.

Large spills should be contained, if possible, within a diked/bunded area. Stacking sand bags or similar material can be used temporarily. Avoid run-off into storm sewers routed to public waters. If possible, the spill should be recovered in appropriate containers for reuse or disposal.

11.3 Air Emissions

Air emissions are restricted and require permits in most locations. Emissions from storage, loading, and unloading facilities may be easily controlled by back venting transport containers to storage tanks through a vapor return line or vapor equalization line. Be careful to avoid contaminating other tank inventories when tanks are connected by a common header or exhaust system piping.

Scrubbing with sodium hydroxide or incineration are also acceptable treatments for methacrylic acid exhaust or vent gas. Spent or depleted scrubber solution must be disposed of properly by biological treatment or incineration.

In the EU, the storage and use of methacrylic acid may fall under the Integrated Pollution Prevention and Control Directive (96/61/EC). As of this writing, methacrylic acid in the U.S. is a SARA Section 312 reportable substance for inventory purposes. It falls under SARA Section 311 hazard categories: acute health, chronic health, reactive, and fire. Although not designated by name as hazardous by Superfund, methacrylic acid falls into its «Ignitable, Corrosive, Reactive» (ICR) category as a corrosive.

Please be aware that these regulations are constantly developing and other regulations may apply. Contact a methacrylic acid manufacturer for the most current MSDS for more complete and up to date information.

12 Appendix

Table 12-1: Key to Symbols in Figures 12-1, 12-2 and 12-3

SYMBOL	DEFINITION
FAL	Flow alarm – low
FE	Flow element
FI	Flow indicator
FIC	Flow indicator/controller
JAL	Power alarm – low
JR	Power recorder
JSL	Power switch – low
JT	Power transmitter
LAH	Level alarm – high
LG	Level gauge
LI	Level indicator
LSHH	Level switch - high high (shuts down unloading pump)
PIC	Pressure indicator and control
PVRV	Pressure and vacuum relief valve
TAH	Temperature alarm – high
TAL	Temperature alarm – low
TC	Temperature control
TE	Temperature element
TI	Temperature indicator
TR	Temperature recorder
TSH	Temperature switch – high (shuts down pump)

Figure 12-1: Example of a Methacrylic Acid Storage Facility
The example illustrates some of the safety features discussed in the booklet.
Not all equipment or instrumentation required for operability is shown.

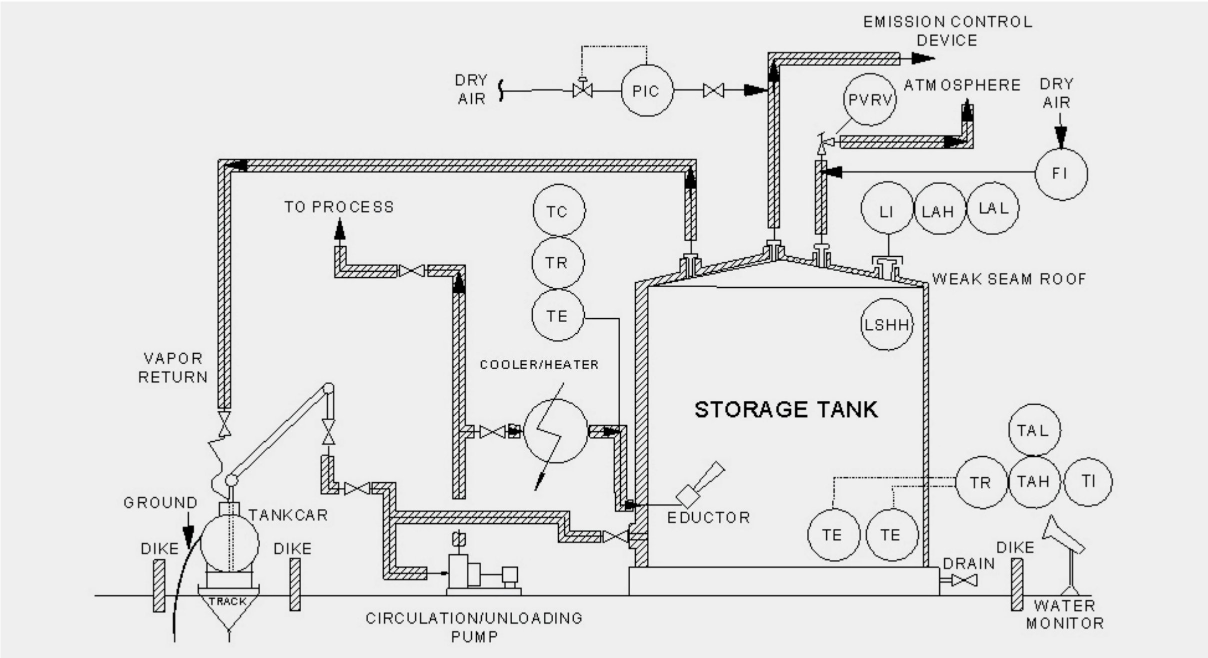


Figure 12-2: Example of a Methacrylic Acid Storage Tank Temperature Control System
This example illustrates some of the safety features discussed in this booklet.
Not all equipment or instrumentation required for operability is shown.

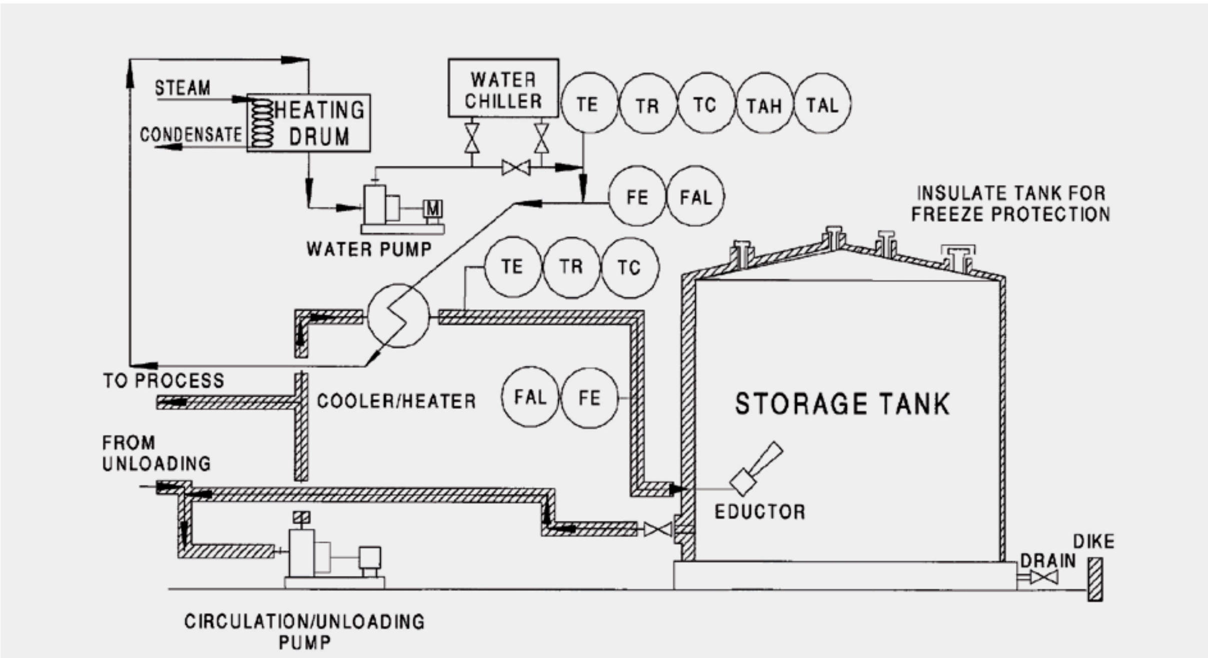
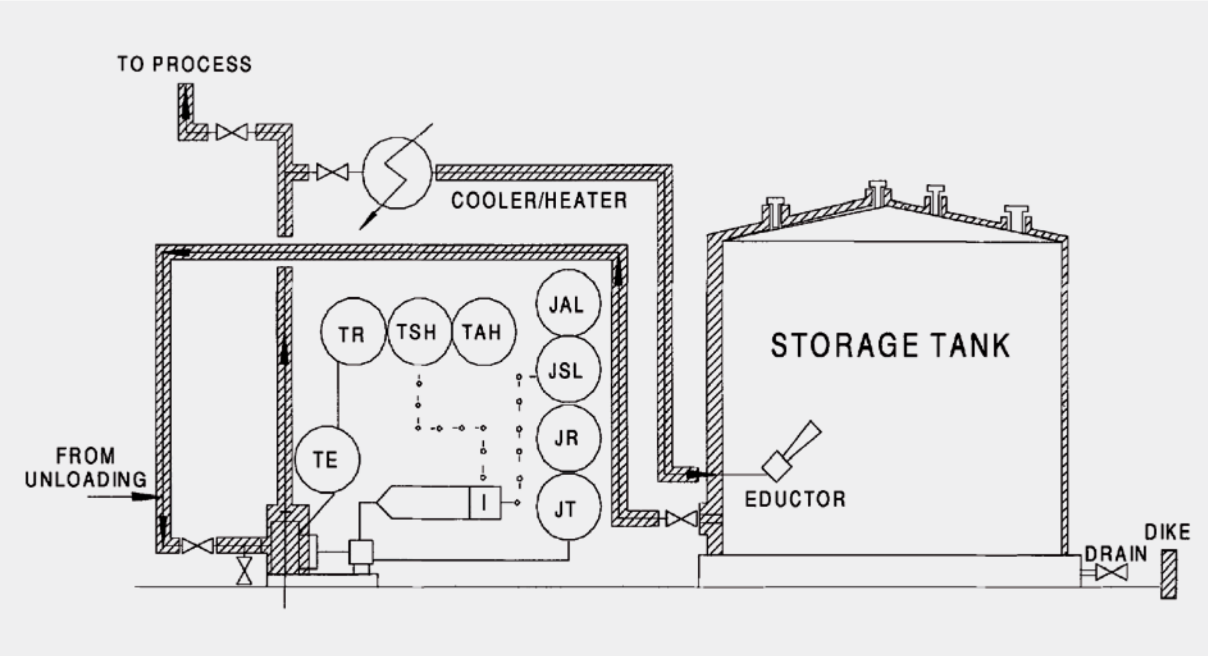


Figure 12-3: Example of a Methacrylic Acid Pump Loop
This example illustrates some of the safety features discussed in this booklet.
Not all equipment or instrumentation required for operability is shown. See Table 12-1 for key to symbols.



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