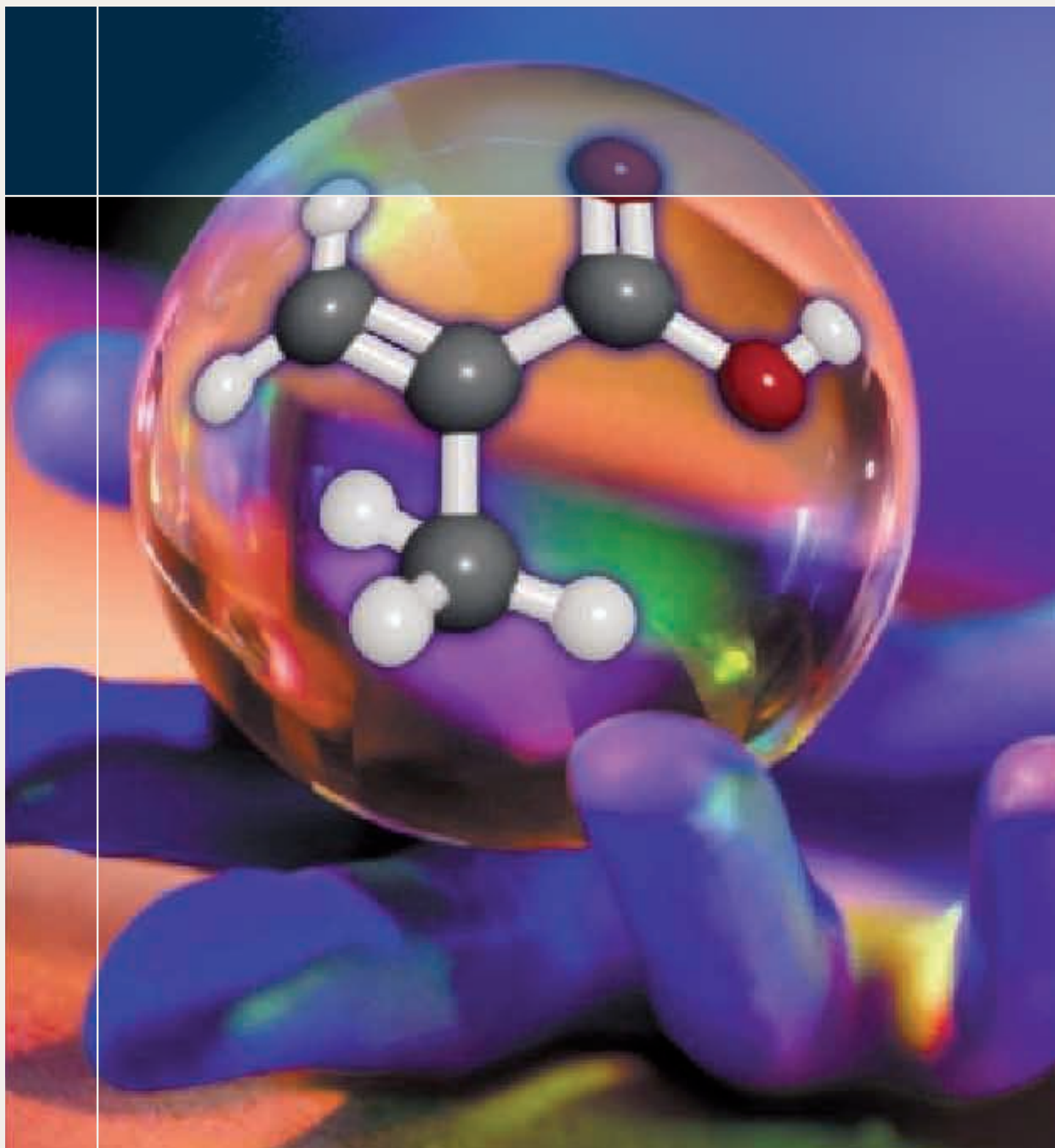


Methacrylate Esters

Safe Handling Manual

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Introduction

This Manual provides general information on the safe handling of the esters of methacrylic acid including: Methyl Methacrylate (CAS Number 80-62-6), Ethyl Methacrylate (CAS Number 97-63-2), n-Butyl Methacrylate (CAS Number 97-88-1), i-Butyl Methacrylate (CAS Number 97-86-9), and 2-Ethylhexyl Methacrylate (CAS Number 688-84-6), 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 the esters of methacrylic acid with a minimum content of 98 percent pure. They conform to specifications reported in the technical information bulletins issued by methacrylate ester 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 methacrylate esters or before designing a storage system for the esters. 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 methacrylate esters users (Methyl Methacrylate, Ethyl Methacrylate, n-Butyl Methacrylate, i-Butyl Methacrylate, and 2-Ethylhexyl Methacrylate) about the unique hazards associated with handling these chemicals and measures to be followed to protect human health, equipment, and the environment. Methacrylate ester hazards include its skin sensitization, 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 labels and Material Safety Data Sheet for methacrylate esters before working with them. Additional information is available in the publication entitled "OECD SIAR Short Chain Methacrylate Esters- Ethyl Methacrylate, n-Butyl Methacrylate, iso-Butyl Methacrylate and 2-Ethylhexyl Methacrylate", pending at time of publication, see http://www.oecd.org/document/63/0,2340,en_2649_34379_1897983_1_1_1_1,00.html. The information in this manual is current as of the date of publication. If you have any questions or need more detailed information, you should contact your methacrylate esters 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 Química, S.A. (Spain), Rohm and Haas Company (United States) and Evonik Röhm GmbH (Germany).

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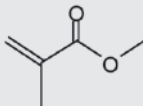
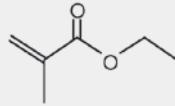
Although MPA and Cefic believe that the information contained in this Manual is factual, it is not intended as a statement of legal requirements with respect to handling methacrylic acid. Consult with legal counsel and/or appropriate government authorities to ensure compliance with local, regional, national, and international laws and regulations. It is the customer's responsibility to ensure proprietary rights and existing laws are observed. No warranty or representation, either expressed or implied, is made with respect to any or all of the content of this document and neither MPA nor Cefic nor its members assume any legal responsibility.

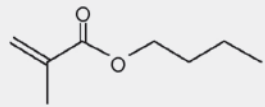
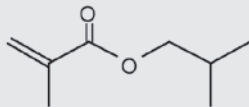
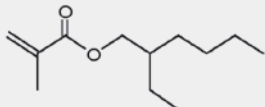
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1 Names

COMMON NAME	METHYL METHACRYLATE	ETHYL METHACRYLATE
CAS NUMBER	80-62-6	97-63-2
CAS NAME	2-Methyl-2-Propenoic Acid, Methyl Ester	2-Methyl-2-Propenoic Acid, Ethyl Ester
UN NUMBER	1247	2277
EEC N°	607-035-00-6	607-071-00-2
SYNONYMS	MMA Methacrylic acid, Methyl Ester Methyl Methacrylate Monomer Methyl, 2-methyl-2-Propenoate	EMA Methacrylic acid, Ethyl Ester Ethyl Methacrylate Monomer Ethyl, 2-methyl-2-Propenoate
EINECS NUMBER	201-297-1	202-597-5
CHEMICAL FORMULA		
STOICHIOMETRIC FORMULA	C ₅ H ₈ O ₂	C ₆ H ₁₀ O ₂
EEC classification	Highly flammable Irritant	Highly flammable Irritant
EEC labeling symbols	Highly flammable (F) Irritant (Xi) R 11-37/38-43 S 24-37-46, note D	Highly flammable (F) Irritant (Xi) R 11-36/37/38-43 S 9-16-29-33, note D
Threshold Limit for Preparations	20%: (Xi) 1%: Irritant (Xi/R43)	20%: (Xi) 1%: Irritant (Xi/R43)
IMDG	Class 3	Class 3
49 CFR, ICAO, IATA Packing Group	II	II
ICAO - CLASS	Class 3	Class 3
ADA/RID ORANGE PLATE	339/1247	339/2277
ADR/RID - CLASSIFICATION	Class 3	Class 3

N-BUTYL METHACRYLATE	ISO-BUTYL METHACRYLATE	2-ETHYLHEXYL METHACRYLATE
97-88-1	97-86-9	688-84-6
2-Methyl-2-Propenoic Acid, n-Butyl Ester	2-Methyl-2-Propenoic Acid, i-Butyl Ester	2-Methyl-2-Propenoic Acid, 2-Ethylhexyl Ester
2227	2283	1993
607-033-00-5	607-113-00-X	607-134-00-4
n-BMA Methacrylic acid, n-Butyl Ester n-Butyl Methacrylate Monomer n-Butyl, 2-methyl-2-Propenoate	i-BMA Methacrylic acid, i-Butyl Ester Iso-Butyl Methacrylate Monomer Iso-Butyl, 2-methyl-2-Propenoate	2-EHMA Methacrylic acid, 2-Ethylhexyl Ester 2-Ethylhexyl Methacrylate Monomer 2-Ethylhexyl-2methyl-2-Propenoate
202-615-1	202-613-0	211-708-6
		
C ₈ H ₁₄ O ₂	C ₈ H ₁₄ O ₂	C ₁₂ H ₂₂ O ₂
Flammable Irritant	Flammable Irritant Dangerous for the environment	Irritant
Irritant (Xi) R 10-36/37/38-43, note D	Dangerous for the environment (N) Irritant (Xi) R 10-36/37/38-43-50 S 24-37-61, note D	Irritant (Xi) R 36/37/38 S 26-28, note A
20%: (Xi) 1%: Irritant (Xi/R43)	20%: (Xi) 25%: (N) 1%: Irritant (Xi/R43)	10%: (Xi)
Class 3	Class 3	Not subject to dangerous goods regulations
III	III	Not subject to dangerous goods regulations
Class 3	Class 3	Not subject to dangerous goods regulations
39/2227	39/2283	N/A
Class 3	Class 3	Not subject to dangerous goods regulations

2 Properties of Methacrylate Esters

2.1 Grades of Methacrylate Esters

The grades of methacrylate esters usually only depend on the type and amount of inhibitor added to the methacrylate ester. Specific information is available upon request from producers.

2.2 Properties and Characteristics of Methacrylate Esters

The values in the following table 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 manufacturer for more up-to-date information.

PROPERTIES	MMA	EMA	n-BMA	i-BMA	2-EHMA
CAS #	80-62-6	97-63-2	97-88-1	97-86-9	688-84-6
Molecular Weight	100.12	114.14	142.2	142.2	198.31
Boiling Point (°C at 101 kPa)	100.5	118.2 ⁷	163	155	227.6 ⁷
Freezing Point (°C)	-48	< -75 ⁷	-50 ⁷	-35 ⁷	< -50 ⁷
Density (g/cc at 20°C)	0.94	0.912 ⁷	0.896 ⁶	0.883	0.885 ⁷
Refractive Index (at 20°C)	1.412	1.4115	1.4211	1.42	1.44 ⁶
Viscosity (mPa-s or cP at 25°C)	0.54	0.53	0.94	0.92	2.4 ⁸
Vapor Pressure (HPa at 20°C) (mmHg at 20°C)	42 ⁷ 32 ⁷	20 15	2.10 ⁷ 1.58 ⁷	2.10 ⁷ 1.58 ⁷	0.065 ⁷ 0.049 ⁷
Flash Point, (Tag Closed Cup, °C)	10 – 11	20-21	49 ¹⁰	41	92 ⁹
Water Solubility (G/100G at 20°C) <i>Monomer in water</i> <i>Water in monomer</i>	1.6 ⁷ 0.99 ⁶	0.469 ⁷ 0.64 ⁶	0.036 (25°C) ⁷ 0.3 ⁶	0.047 ⁷ 0.3 - 0.4 ⁶	0.00016 (25°C) ⁷ 0.14 ⁶
Explosive Limits (101 kPa, 760 mmHg) <i>Lower</i> <i>Upper</i>	2.1 12.5	1.8 9.6	2 ¹ 8 ¹	1 7.4	
Latent Heat of Vaporization <i>KJ/Mole</i> <i>Kcal/Mole</i>	39.5 9.4	40.6 9.7	50.0 11.9	47.2 11.3	
Heat of Polymerization (KJ/Mole)	54.0 ³	59.1 ⁶	56.6 ⁶	59.9 ⁶	
Specific Heat (20-30°C) <i>KJ/Kg-°K</i> <i>Cal/g-°C</i>	1.90 0.45	1.70 0.41	1.97 0.47	1.89 0.45	2.01 ⁶ 0.48 ⁶
Partition Coefficient <i>Log Pow (Octanol/Water) 20°C</i> <i>Henry's Law Constant (Pa-m³/mol at 20°C)</i>	1.38 ⁵ 25-34 ⁵	1.87 ⁷ 14-85 ⁵	2.99-3.03 ⁷	2.99-3.03 ⁷	4.95-5.59 ⁷
Autoflammability (°C)	435	370	294	390	
Tg of Polymer (°C)	105 ⁶	65 ⁶	20 ⁶	48 ⁶	-10 ⁶
Odor Threshold (ppm)	0.2 ⁴	0.17 ⁸	0.016 ²	0.07 ⁸	0.76 ⁸

1 Chemical Properties Handbook

2 Storage and Handling of Acrylic and Methacrylic Esters and Acids, Rohm & Haas, December 1987

3 Heats of Polymerization of Acrylic Acid and Derivatives, Evans and Tyrrell, Journal of Polymer Science, Vol 2, No 4, 1947

4 Handbook of Environmental Data on Organic Chemicals, Karel Vershuers

5 http://www.dep.state.pa.us/physicalproperties/_cgi-bin/PPP_Search.idc

6 San Esters Corp. (www.sanesters.com)

7 SIDS Initial Assessment Report, Methacrylates Producers Association, 2004

8 ICI Product Bulletin, April, 1994

9 Polymer Handbook, 4th Edition, Wiley & Sons

10 Penske Marten Closed Cup

3 Training and Job Safety

Many of the methacrylate esters are considered to be hazardous under the Occupational Safety and Health Administration's (OSHA) Hazard Communication Standard (29 CFR 1910.1200) and the current EU Classification Packaging and Labeling of Dangerous Substances Regulations. Therefore, all employees must be provided with adequate health and safety information and training to handle the methacrylate esters. The training requirements have been spelled out in the Hazard Communication Standard and the EU Directive.

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

4 Instability and Reactivity Hazards

4.1 Polymerization

Methacrylate esters are highly reactive. Polymerization of methacrylate esters can be very violent, involving considerable heat and pressure and ejecting hot polymer and monomer from the site of polymerization. Generally the lower molecular weight esters will produce a higher hazard. Therefore MMA, n-BMA, i-BMA, & EMA are more hazardous than 2-EHMA in the event of an uncontrolled polymerization.

An explosion hazard exists if the material is in a closed or poorly vented container because pressure build-up can occur very rapidly. Typically, methacrylate esters contain stabilizer levels that provide a shelf life of about 6 months at ambient conditions and should be used within that time. Exceptions do exist; your supplier should be contacted for shelf life information for the specific monomer and grade purchased. Commercially available methacrylate esters are inhibited with stabilizers including: monomethyl ether of hydroquinone (MEHQ, CAS 150-76-5), also known as para-methoxyphenol (PMP) and 4-Hydroxyanisole (HA). Other inhibitors include: hydroquinone (HQ, CAS 123-31-9), 2,4-Dimethyl-6-tert-butylphenol (BDMP, DMTBP or Topanol-A®/AO30®/IONOL K78®, CAS 1879-09-0), and 2,6-Di-tert-butyl-4-methylphenol (BHT/ Topanol-O®, CAS 128-37-0) and others, which prolong the usable shelf life.

NOTE: Some of these stabilizers are available under alternative trade names. However, concentrations can vary and it is essential that the concentration of the active stabilizer is taken into account when determining the amount required in order to achieve the required stabilizer level in the product.

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

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

4.1.1 Overheating and Photo-initiation

Commercially available methacrylate esters are inhibited with MEHQ, HQ, 2,4-Dimethyl-6-tert-butylphenol (Topanol-A®/AO30®/IONOL K78®), and 2,6-Di-tert-butyl-4-methylphenol (BHT or Topanol-O®) that prolongs the usable shelf life. However, this usable shelf life is reduced exponentially with increasing temperature. Therefore, exposure to heat must be avoided. Maintain the temperature of methacrylate esters below 40°C (104°F), preferably below 30°C (86°F). Only store drums in the shade; do not store methacrylate ester drums in the sun. Avoid extreme temperatures such as storage next to steam pipes or storage in warm rooms. Normal ambient temperatures encountered for bulk storage at any location are generally satisfactory for maintaining stability within the recommended maximum shelf life (maximum storage time).

Methacrylate esters can polymerize as a result of photo-initiation. Where sight glasses or other transparent sections are needed for visual observation in methacrylate esters service, they should have covers to exclude light between observations.

4.1.2 Contamination

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

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

4.1.3 Corrosion

Corrosion in general can also pose a polymerization hazard. Metal ions such as iron and copper can initiate polymerization. Metal ions result if there is corrosion in the storage or transportation system. Corrosion can be caused by using an improper material of construction, accidental introduction of incompatible metals into the system such as leaving a non-sparking tool in a storage tank, or the contamination of the methacrylate esters with materials such as acids that are corrosive to normal methacrylate ester 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.

4.1.5 Inhibitor Deactivation/Oxygen Depletion

Dissolved oxygen is necessary for inhibitors to function effectively, acting as the initial, and very efficient, radical scavenger. Methacrylate esters should therefore 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 some of the methacrylate ester vapors in air form flammable mixtures at room temperature, it may be desirable to use a nitrogen/oxygen gas mixture with less than 21% by volume of oxygen to avoid flammability. However, the atmosphere above the monomer should contain at least 5% oxygen to maintain inhibitor effectiveness.

Oxygen is consumed slowly as part of the free radical scavenging mechanism. Thus, the atmosphere above methacrylate esters in a closed system should be periodically replenished with air or nitrogen/oxygen gas mixture of 5-21% by volume of oxygen. Large volumes in vessels open to the atmosphere should be gently circulated. Residues in transfer lines and other stagnant areas should be blown out with a 5-21% oxygen-containing gas mixture, or should be designed to be self-draining.

4.2 Polymerization Detection

Methacrylate esters have 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. In that event, exercise caution, but if a sample can be safely acquired, it can be used to test for the presence of soluble polymer to confirm polymerization. While presence of soluble polymer confirms an ongoing polymerization, inconsistent sampling can give a false negative result that does not prove anything until all the other indicators (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.

Occasionally on the plant scale, uncontrolled methacrylate ester polymerizations proceed slowly. Therefore, 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 whether a polymerization is underway before temperature extremes are reached.

See Section 5. Response to Uncontrolled Polymerization for more information.

CAUTION

Even slow polymerization has the potential to accelerate into a runaway reaction. If the temperature rises above 45°C (113°F) or 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 or the temperature reaches 55°C (131°F), the situation is critical.

4.3 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 polymerization of condensed monomer vapors which are likely to be uninhibited), high temperatures and pressures can build up over time. If the temperature reaches approximately 195-200°C (383-392°F), methacrylate esters will undergo degradation. Some evidence exists that methacrylate esters can undergo decarboxylation at approximately 195°C (383°F) generating carbon dioxide. With a 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 methacrylate esters have been reviewed by the Manufacturers. 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 methacrylate esters 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 methacrylate esters without prior emergency planning. Never approach a container of uncontrolled polymerizing methacrylate esters after it has reached 55°C (131°F) or if the rate of temperature rise has exceeded 5°C/ hour (9°F/hour) with no external heat source. **Consider this for all response choices.**

The most effective response to an uncontrolled polymerization of methacrylate esters is the remote addition and mixing of shortstop inhibitor, phenothiazine (PTZ). 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 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.
- Apply cooling water to the exterior of the vessel to reduce the temperature of the methacrylate esters. 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.
- Do not attempt to mix the contents of the container unless shortstop inhibitor has been added to the methacrylate esters. 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 (131°F) 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. Handlers of methacrylate esters should maintain a supply of PTZ for use when needed. MEHQ, HQ and AO3o are not shortstop inhibitors. MEHQ, HQ or Topanol A / AO3o can effectively extend the shelf life of methacrylate esters only if there is adequate oxygen in solution. Temperatures significantly above ambient may deplete the oxygen in solution and prevent MEHQ, HQ and AO3o from working. Temperatures reached during a runaway polymerization will defeat the functionality of MEHQ or HQ. MEHQ, HQ or AO3o will not have a significant impact if added to a runaway polymerization of methacrylate esters.
 - If impact to the environment and to personnel exposures is acceptable, consider draining the contents of the container into a diked/bunded area. In this case, vapor release that could cause pressure if contained is now vented directly to the atmosphere and thus protects the vessel. Fire fighting foam can be used to slow vapor release and control exposures and risk of fire.
 - Consider moving a mobile container away from people and equipment; barricading of drums/IBC/totes or totes/IBC is another option.

NOTE: A vessel undergoing an uncontrolled polymerization may experience high enough temperature to cause venting. 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 Health Concerns

6.1 Toxicity

The principal acute hazards of methacrylate esters (MMA, n-BMA, i-BMA, EMA, and 2-EHMA) are the propensity of the liquid and vapors to be irritating to mammalian tissue.

Direct contact may cause irritation of the eyes, skin, nose and throat. Direct contact with skin may also result in the development of skin allergy, in which future exposures can cause itching and skin rash.

Although ingestion is not a typical route of exposure to chemicals in the industrial environment, methacrylate esters are mildly toxic by ingestion, but may cause irritation of the mouth, throat, esophagus, and stomach.

Inhalation of high concentrations of vapors or mists of methacrylate esters will cause irritation of the respiratory tract and may cause dizziness, lightheadedness, and may even cause someone to pass out. Inhalation of lower concentrations may produce mild irritation of the respiratory tract.

Various regulatory and occupational health authorities have established exposure limits for the methacrylate monomers. See Section 6.3 Industrial Hygiene for more information. Your supplier's current label and MSDS should be consulted for current toxicological information.

6.2 First Aid

In order to minimize adverse consequences of methacrylate esters incidents, all personnel assigned to work with methacrylate esters 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 eye wash stations.

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.

6.2.1 Contact with the Eyes

If even minute quantities of methacrylate esters 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. 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 ordered by the physician.

6.2.2 Inhalation

Personnel affected by methacrylate esters 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.

6.2.3 Contact with Skin

The emergency safety shower should be used immediately to remove methacrylate esters. 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 methacrylate esters from the skin and reduce injury. After showering, get immediate medical attention. No salves or ointments should be applied 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.

6.2.4 Ingestion

Although ingestion of chemicals is rare in the industrial setting, in the event of methacrylate esters ingestion the affected individual should be made to drink large quantities of water. Activated charcoal may be administered. Do not induce vomiting. Consult a physician.

If the affected individual is unconscious or having convulsions keep the affected individual warm. General rules of first aid and resuscitation apply under avoidance of self-contamination. 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.

6.3 Industrial Hygiene

Exposure to methacrylate esters 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. Workplace testing is recommended to determine exposure levels and the personal protective equipment (PPE) needed. When high exposures are revealed, corrective measures must be taken.

Occupational health standards-setting organizations in many countries have set work place exposure limits for some of the methacrylate esters. Consult your supplier's MSDS for the most current occupational standards for these compounds. Some typical examples of international occupational standards are given on the next page.

These workplace exposure limits are time-weighted average (TWA) values. In general for a TWA value of 25 ppm short exposures in excess of 25 ppm are permitted providing that there are offsetting periods below 25 ppm such that the overall exposure averages 25 ppm or less for the 8-hour workday. However the exposure over a 15-minute period must never exceed the short-term exposure limit (STEL) and it should be recognized that short duration, peak exposures, in excess of the STEL, may be overtly irritating to the respiratory system. Effectiveness of PPE and other exposure controls can only be verified by workplace exposure measurements.

Given that many of the higher esters do not have exposure limits set at the present time, it would be prudent to adopt an exposure limit similar to MMA.

International Occupational Exposure Standards (as of November 2007)

PRODUCT	COUNTRY	TWA OR EQUIVALENT (8-HOUR)	STEL
MMA	Netherlands	10 ppm	150 ppm 100 ppm 100 ppm 200 ppm 100 ppm
	Denmark	25 ppm	
	Norway	25 ppm	
	Sweden	50 ppm	
	UK	50 ppm	
	Germany	50 ppm	
	USA (ACGIH)	50 ppm	
	USA (OSHA)	100 ppm	
	France	100 ppm	
EU IOELV (proposed)	50 ppm		
EMA	Netherlands	10 ppm	75 ppm
	Denmark	25 ppm	
	Norway	50 ppm	
	Sweden	50 ppm	
n-BMA	Netherlands	10 ppm	75 ppm
	Denmark	25 ppm	
	Norway	50 ppm	
	Sweden	50 ppm	
i-BMA	Netherlands	10 ppm	75 ppm
	Denmark	25 ppm	
	Norway	50 ppm	
	Sweden	50 ppm	

6.4 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 methacrylate esters. 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 PPE procedures. The hazard of each task must be thoroughly assessed, appropriate PPE must be selected, and training in the correct use, care and limitations of the PPE must be provided.

Methacrylate esters, particularly the lower molecular weight compounds, permeate quickly through many common glove materials. The most appropriate glove depends on consideration of a number of factors including the physical strength of the glove, the degree of manual dexterity required, the amount of permeation through the glove material, the duration of wear, and perhaps the cost of the glove.

There are a wide variety of elastomeric and laminate gloves available. Common elastomeric glove materials include latex (natural rubber), neoprene (polyisoprene), nitrile rubber (ABS rubber), butyl rubber, polyvinyl alcohol (PVA), polyvinyl chloride (PVC), and fluoroelastomers. Laminate gloves are made from heat sealed sheets of PVA between layers of polyethylene.

In permeation tests PVA/Polyethylene laminate and supported PVA gloves performed best (note that PVA can be rendered ineffective by contact with water if the laminate layer is breached). Butyl and nitrile rubber gloves offer short-term protection. Latex «surgical» gloves offer little protection. Contact your supplier for the latest information on glove materials.

Gloves should be stored correctly and changed regularly, especially if excessive exposure has occurred.

6.4.1 All Personnel

All personnel who are in the general area where methacrylate esters are being handled should wear appropriate PPE. This protective equipment should be worn even if an individual is not planning to come in contact with the methacrylate esters processing equipment. An anti-statically finished working garment is recommended.

6.4.2 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, safety shoes, and chemical splash goggles. Depending on the situation, consider wearing chemical-resistant boots if walking surface contamination is anticipated. In addition, air-purifying respiratory protective equipment should be worn if air monitoring has demonstrated that airborne concentrations of methacrylate esters are above the exposure limit.

6.4.3 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 PPE: chemical-resistant suits, chemical-resistant boots and gloves, and chemical splash goggles. Wear a face shield and/or chemical resistant hood in the event of opening drums or lines that may be under pressure. Air-purifying respiratory protective equipment may be worn if airborne concentrations of methacrylate esters are above the exposure limit. For high concentrations a supplied-air respirator is required.

6.4.4 Emergencies

Any time there is a risk of exposure to airborne concentrations of methacrylate esters 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, chemical-resistant suits, chemical-resistant boots, hardhat, and chemical splash goggles.

In the event of a release of methacrylate esters, 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 appropriately stored outside of, but near, the area where the methacrylate esters are used.

7 Fire and Explosion Hazard

All methacrylate esters with the exception of 2-EHMA can form readily ignitable vapours at ambient temperatures. Methacrylate esters are typically handled at ambient temperature. The flash points and other flammability characteristics are listed in Section 2.2. Ignition sources can be spark discharges from static electricity or any other source. Ignition may also occur, if excessive amounts of mist or aerosol have formed in the air. Vapors are heavier than air and may travel a considerable distance to a source of ignition and flash back. Containers may explode in fire or when heated because of polymerization.

All methacrylate esters are immiscible in water. Consequently water may be ineffective to fight a fire. However if a fire occurs in or close to a tank farm containing methacrylate monomers, tanks and pipes should be cooled to prevent monomers from polymerizing by spraying with plenty of water. Effective fire extinguishing agents include dry chemical, foam, and carbon dioxide.

During transfer between containers, the containers must be electrically interconnected (bonded) and properly grounded/earthed. Splash filling into a tank must be avoided. 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, 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.

The low flash points of the lighter methacrylate esters require that all permanent storage tanks be fitted with the legally obligatory fire protection equipment. Outlets into the atmosphere may require flame arrestors and detonation traps should be considered for manifolded vents, particularly if the vent is connected to an ignition source, such as a thermal oxidizer or flare. In case of fire, evacuate non-essential personnel to a safe location. Carbon dioxide or dry chemical extinguisher may be used on fires. Water spray, fog or "alcohol" or universal-type foam may be used on large fires.

Containment of runoff of fire fighting materials should be planned as required by regional, country, state or local authorities. See Section 6.4.4, Emergencies, for PPE to be worn for all emergencies. Also use appropriate PPE during fire fighting.

7.1 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.

Do not cut, drill, grind, or weld near drums/IBC/totes. The heat from such work could ignite residual material in the drum/IBC/Tote. Residual vapors in drums or containers may explode on ignition. Improper disposal or reuse of drums/IBC/totes may be dangerous and/or illegal.

A wet scrubber using an aqueous caustic solution with organic amines can efficiently treat methacrylate ester vapors. For the final off gas purification, an active carbon cartridge can be used if protected from high organic loading. The heat of adsorption on active carbon is unusually high for all methacrylate monomers. Therefore, if highly loaded exhaust gases come into contact with active carbon, ignition is likely to occur.

CAUTION

Active carbon cartridges must never be used for the removal of methacrylate esters from exhaust gases, unless the gases are pre-treated, e.g., in a wet scrubber.

For the prevention of a back flash into the tank, carbon cartridges must always be isolated from the bulk storage tank by a flame suppression system (i.e., flame arrestor, scrubber, etc).

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

8 Storage and Handling

The stability of methacrylate monomers and the proper methods for handling methacrylate monomers safely are determined by the following factors:

- Toxicity (see Section 6.1)
- Dissolved oxygen (see Section 4.1.5)
- Effectiveness of inhibitors and the storage life of monomers at various temperatures
- Flammability
- Effect of materials of construction on the stability and other properties of monomers.

Other important stability and safety factors include the physical and chemical properties of the monomers, their odors, their impact on the environment, their sensitivity to environmental conditions, light and the presence of a water layer (commercially supplied inhibitors are more soluble in water, and therefore, tend to diffuse out of the monomer phase and into the aqueous phase, rendering the monomer uninhibited). Please read this entire Manual before storing methacrylate monomers or before designing a storage system for methacrylate monomers. All preventive measures described in this Manual must be followed to minimize the possibility of violent polymerization. See Section 4, Instability and Reactivity Hazards, for a description of the polymerization hazards.

8.1 Drum/IBC/Tote Storage

Methacrylate monomers are sold in steel or HDPE drums. In some regions of the world, reusable stainless steel drums may be used. IBC/totes of various constructions (including ultraviolet radiation protection) may also be used and should be treated similarly to drums. Drums/IBC/totes should be electrostatically safe due to the flammability of the materials being stored.

In order to ensure inhibitor effectiveness, drums/IBC/totes are initially filled so that a vapor space containing sufficient oxygen is maintained. Oxygen is consumed slowly as part of the free radical scavenging mechanism. Consult your supplier for the drum/IBC/tote shelf life.

- The drums/IBC/totes must be stored according to applicable national, state and local regulations. Lacking other guidance or limits, drums/IBC/totes 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. Avoid any exposure to the heat of direct sunlight. Warehouses must be well ventilated.
- If sheds are used for the outdoor storage of drums/IBC/totes, they should be constructed of non-combustible material, be well ventilated and shield the drums/IBC/totes from the sun. They should also conform to the applicable requirements of underwriters and insurance companies.
- Avoid exposure to elevated temperatures.

8.1.1 Drum/IBC/Tote Handling

When a carload or truckload of drums/IBC/totes is received, open the doors carefully. Leave the doors open for a while to allow any potential odors to dissipate before entering. If a strong, persistent odor is present, indicating a leaking container, immediately call the supplier. See Section 10.2, Spill and Leak Control.

8.1.2 Drum/IBC/Tote Emptying

Before drums/IBC/totes are opened, they must be supported and grounded/earthed as well as bonded to the pipe and pumping equipment. A static-free dip pipe or flexible stainless steel hose must be used to drain the monomers. Operations should be conducted with adequate local exhaust ventilation to minimize personnel exposure and the dangers from spillage and the escape of vapors.

Drums/IBC/Totes and fittings should never be struck with tools or other hard objects that may cause sparking or puncture. Use non-sparking hand tools when opening flammable monomer drums/IBC/totes.

An overhead vapor space must be maintained in the drums/IBC/totes to provide additional oxygen for polymerization inhibition and to prevent over-pressuring of the drums/IBC/totes. Do not use an inert gas, such as nitrogen, as a vapor pad on the drum/IBC/tote.

NOTE: Drum contents may be under pressure or vacuum.

When removing plugs (bungs) from a drum of methacrylate monomers (or opening an IBC/Tote), the operator should wear PPE recommended in Section 6.4, 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.

Pumping is the best method to empty drums/IBC/totes. Note that electric pumps must comply with the area electrical classification. Drums/IBC/Totes may be emptied by gravity using self-closing valves. Do not use pressure to displace drum/IBC/tote contents.

Do not cut, drill, grind, or weld 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 drums/IBC/totes may be dangerous and/or illegal.

8.1.3 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 the methacrylate ester and then rendered unusable by crushing or piercing. Dispose of rinse water properly. See Section 10.1, Waste Disposal.

8.2 Bulk Storage

Methacrylate monomers must be stored under an atmosphere containing 5-21% oxygen. 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 methacrylate monomers imply higher risk because of higher potential consequences. Methacrylate monomers are normally stored at ambient temperatures. Equipment should be installed for effective monitoring of temperature and appropriate alarms to warn of possible unscheduled polymerization events. An effective maintenance plan, including control devices, is critical. 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.

The optimum capacity for a storage tank is a function of the volume and frequency of deliveries of monomer and the monomer throughput. For the most efficient scheduling of deliveries, storage tanks should have a minimum capacity of 1.5 times the volume of an expected delivery. The best design for an aboveground tank incorporates a vertical shell, a flat bottom and a conical top. The design selected should allow uniform mixing of the contents with new deliveries. The tank is set on a concrete pad with a concrete dike of sufficient capacity. A tank well with a bottom drain line through the tank pad is needed to provide complete tank drainage.

Tanks normally used for methacrylate ester storage should be painted white or insulated to minimize heat absorption during the summer months. Tanks should be electrically grounded and effectively bonded to connected equipment.

For environmental and regulatory reasons, tanks and pumps should always be positioned in a diked/bunded area. All applicable regional, national, state and local governmental regulations must be observed.

8.2.1 Pressure Relief

There is no guaranteed or warranted method for relieving the pressure from a methacrylate ester runaway polymerization 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. Emergency venting devices normally used for flammable liquids are considered to give adequate fire protection; however this type of device will not provide adequate relief in the event of an uncontrolled or runaway polymerization.

For the natural breathing of the tank, a conservation valve should always be installed. Various designs, such as weighted pallet 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 methacrylate ester vapors can condense 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, to prevent interference with their proper operation. Relief valves and nozzles can be electrically traced and insulated to help control polymer formation by preventing condensation.

A vent line and associated devices are required to prevent corrosion and polymerization by providing a blanket of dry, oxygen-containing atmosphere over the monomer, to dispose of vapors and to reduce fire hazard and odor. If a dryer or overflow pot is used, it should be checked frequently for plugging by polymer from condensed uninhibited monomer.

A drying agent can be used to provide a dry vapor space over the monomer to eliminate water contamination. It can be installed on the vent line, pad gas line, or conservation valve inlet line. The drying agent is usually renewed every 3 to 6 months, depending on local climatic conditions. Care should be taken to prevent blocking due to polymer. Alumina, molecular sieves, and calcium chloride are typical desiccants.

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

8.2.2 Temperature Measurement

Redundant temperature-sensing elements should be installed. A temperature alarm should also be installed as a monitor and safeguard to warn of polymerization. At least two independent temperature-sensing elements (thermocouples) should be installed near the tank bottom to ensure that they are always submerged in the liquid. In larger tanks it is sometimes advantageous to have a second pair of sensors installed above the lower third of the total tank height.

The temperature monitoring system should 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. If an alarm is used, it should activate at a temperature about 5°C above the normal maximum temperature of the stored liquid.

8.2.3 Level Instruments

A steel or stainless steel differential pressure transmitter purged with dry, oxygen-containing gas is preferred as the level-measuring device. This will provide continuous level readout, at any remote location, with alarm capabilities. A high level alarm at 85 - 90% of the tank capacity is suggested, coupled with a high level switch set at 90 - 95% which should close a valve on the tank feed line. An ultrasonic type switch is preferred; float switches tend to have problems with plugging from condensed uninhibited monomer that has polymerized. A capacitance probe would be a secondary choice. Manometer-type level gauges or equivalent are preferred over gauge glasses, should the differential pressure style not be used.

8.2.4 Pumps and Transfer Lines

Care must be taken to ensure that pumps and transfer lines 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, self-priming centrifugal pumps, or seal-less pumps (such as magnetic coupled or canned motor pumps with external cooling) are appropriate for transfer service for methacrylate monomers. Mechanical seals are typically used. Centrifugal pumps either packed or with a gliding disk seal, may require more maintenance due to the poor lubrication properties of the methacrylate monomers. For magnetic drive or canned pumps, a temperature sensor must be installed within the pump body. Canned motor pumps and cooled pumps with magnetic coupled drive 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 or level control device should always be installed to protect pumps from dry operation or dead heading.

CAUTION

If seal-less or canned pumps are used, heat generation can cause polymerization in the pump if flow is stopped.

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. Centrifugal pumps present the potential for dangerous splashes if methacrylate monomer leaks through pump seals or glands. Therefore, pump glands, flanged fittings, and valve stems should always be provided with splash collars.

Piping should be cleaned of all grease and scale that may be adhering to the inner walls, after installation. All pipes should be painted white or otherwise protected from the heat of direct sunlight. All pipes should be pitched to drain and have no dead-legs. Pipelines and associated systems that will be dormant should be drained and cleared. Any monomer remaining in the lines may polymerize rapidly.

CAUTION

Inert gas (nitrogen or other non-oxygen containing gas) should not be used to blow pipelines clean. A mixed gas with at least 5% oxygen should be used to clear lines. If flammability protection is desired the mixed gas should be less than 10% oxygen; 8% oxygen is preferred. Care should be used when blowing flammable material lines with air. If static charges develop, an ignition could occur. Some regulations forbid the use of air pressure to move flammable liquids. Thermal expansion of liquid in blocked lines can develop substantial pressure resulting in damage and spills. Use care in designing your systems to avoid these potential problems.

To limit vapor emissions during monomer transfers, it is advisable to use a vapor return line to allow the exchange of monomer vapors between the vapor space 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.

8.2.5 Materials of Construction

Preferred construction materials for tank, pump and pipe installations are steel or stainless steel. Polyethylene, polypropylene, or fluoropolymers are also suitable as materials of construction for methacrylate monomers and may be useful for accessory equipment such as gaskets and valve parts. Rust particles or other particulate matter can be satisfactorily removed from monomers by means of a white cotton fiber or polypropylene wound on a stainless core, or stainless steel mesh cartridge filter. Note: Cotton has been known to shed small fibers. Choose materials carefully.

9 Shipping

9.1 General

Governmental regulations prescribe how to package, mark, label, placard and describe materials on shipping documents, depending on the quantity and type of hazardous material and the method of transport. Employees shipping, receiving and unloading hazardous materials must be trained in the proper application of these regulations.

Methacrylate esters must be shipped with an oxygen-containing atmosphere to maintain inhibitor activity. Pure oxygen or any inert gas should not be used for sparging, blowing lines, or blanketing. Pure oxygen lowers the flash point, thus increasing flammability. Inert gases can reduce dissolved oxygen sufficiently to inactivate inhibitor and cause a polymerization. Air or a gas mixture of 5 to 21% by volume oxygen is preferred when handling methacrylate esters.

Cleanliness of the transport vessels is essential to prevent contamination that can cause polymerization. Rail cars, trucks and isotanks used in other service should be cleaned and dried before reuse and should be free of polymer. Containers must be free of contamination before loading to avoid polymerization of the entire contents.

Maintain vapor space in filled containers and drums sufficient to comply with shipping regulations and to maintain inhibition.

Retained samples should be stored in a cool, dark place for no longer than one year. Amber glass bottles reduce UV initiated polymerization and are recommended for storing small amounts of methacrylate esters.

Protective caps on discharge pipes must be removed with particular care because the pipes may be filled with monomer if the bottom valve of the container leaks.

9.2 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 (Canadian Transport Emergency Centre operated by Transport Canada [<http://www.tc.gc.ca/canutec/en/menu.htm>]) in Canada at (613)996-6666 or CHEMTREC (CHEMical TRansportation Emergency Center [<http://www.chemtrec.org>]) in the US at (800)424-9300.

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.

9.3 Unloading Site

Facilities and policies must foster prompt detection of and response to abnormal events. Unloading should be continuously monitored until completed. Storage tanks high-level alarms should be audible in the unloading area. Automatic shutoffs can prevent overfilling of storage tanks. Storage tanks with high-level shutoffs should be periodically tested to verify proper operation. Unloading at night is discouraged. When it is necessary to unload at night, proper and adequate lighting should be provided in the working areas to control unloading hazards.

Adequate facilities and procedures to handle leaks and spills are essential. An emergency shower and eyewash must be provided, directly accessible to the loading and unloading area. Other sources of water should be available to wash down minor spills. PPE should be worn as suggested in Section 10.3. Unloading areas should have containment to collect and control spills. Drainage should be directed away from the unloading area. Installation of a collection pit as a containment for spills is recommended.

Ergonomic and physical safety must be considered in design of unloading sites. The unloading area should have stairs and a platform if access to the top of the tank truck or railcar is required. Facilities should consider the need for fall arresting systems. Overhead unloading hoses or arms should be counter-balanced to avoid lifting injuries.

Equipment should be appropriately designed for unloading, including:

- A grounding cable must be attached to bulk containers before and during unloading to prevent ignition due to static discharge.
- Unloading piping should be arranged so that the material drains toward the storage tank when transfer stops.
- Unloading areas should be of noncombustible construction. The unloading area should be designed and arranged so that the truck is driven into and off the pad in a forward direction, without having to back equipment into position.
- Packing and lubricant for pumps, glands, etc. must be of a material compatible with methacrylate ester handling.
- Pumping from containers is highly recommended/preferred.
- Never use inert gas.
- A dedicated unloading hose should be used to avoid contamination. A regular physical inspection cycle to examine hose gaskets, cleanliness, and exterior condition is recommended. Periodic pressure checks or replacement can also help assure hose integrity.

Personnel should wear the following PPE whenever making or breaking connections, including bulk unloading:

- Chemical resistant splash suit.
- Chemical resistant gloves.
- For added protection against chemical exposure, chemical resistant boots or overshoes can be worn over leather safety shoes.
- Eye protection of safety glasses with side shields; chemical goggles and/or face shield and NIOSH-approved respiratory protection.

9.4 Shipment Unloading

The preferred method to control odors and flammable vapors of methacrylate esters from tank trucks and rail cars is a closed loop (vapor balanced) system. Displaced receiving tank vapors are returned to the tank truck or directed to vapor control equipment such as scrubbers, thermal oxidizers, or flares.

Do not use compressed air to unload flammable liquids such as MMA. NEVER use gas exceeding 21% oxygen to unload or handle flammable liquids. Pure oxygen lowers the flash point, increasing the risk of fire. Use the minimum pressure necessary to accomplish unloading, never more than 80% of the tank truck's safety relief valve setting. Vapor control equipment such as a scrubber, thermal oxidizer, incinerator or flare may be necessary to treat displaced tank vapors when using pressure unloading.

The following unloading procedures are suggested for methacrylate esters to reduce risk of spills, odors and fires.

Prior to connecting or unloading any shipment, the contents should be verified and unloading equipment should be prepared. Some recommended steps include:

- Positively verify contents by sampling, verifying the bill of lading description, placard verification, and/or other means.
- Locate and test the operation of the nearest emergency shower and eye wash.
- Place warning signs or cordon off unloading area to restrict personnel entry.
- Inspect and wear required Personal Protection Equipment [PPE] before sampling or making any pipe connections to the truck.
- Visually inspect shipping containers for leaks and other irregularities. US DOT forbids vehicles to use public roads after a leak is discovered. Arrangements must be made to stop a leak before the tank truck or rail car can be returned.
- Verify that the receiving vessel can hold the entire shipment.
- Verify that the intended piping and valve alignments will transfer the methacrylate ester to the proper tank. Transferring to the wrong tank will contaminate it and may cause a chemical reaction.
- For tank trailers, spot the trailer, shut off the engine, set the brakes, have the driver leave the unloading area, and set wheel chocks.
- For rail cars, spot the car, set the hand brake, set wheel chocks, place "Tank Car Connected" sign on track, and place derailleurs or lock out switches beyond accessible ends of the rail car.
- Ground the tank trailer or rail car.
- To prevent personnel exposure, verify that all valves are closed before removing any caps, plugs, or flanges.

Some recommended steps for unloading a tank truck or rail car include:

- Connect the appropriate line to the vent valve on the shipping container and connect the vapor return hose.
- Open the vent valve on the shipping container to equalize the shipping container pressure with the receiving tank, pressure source, or atmosphere. To prevent implosion of the shipping container do not unload with the vapor valve closed.
- Connect the liquid unloading hose to the shipping container's unloading fitting.
- Open the unloading valve(s) on the shipping container. On tank trucks this is often an external (secondary) manual valve and an internal valve operated by a hydraulic hand pump.
- Start the pump.
- Monitor hose connections and piping for leaks. Stop transfer if leaks occur. Check that level in receiving tank rises appropriately. If using vapor return, prevent implosion of shipping container by monitoring pressure gauge to assure vapor return line is clear and flowing. Remain in the unloading area until transfer is complete.
- When the container is empty, shut off pump.
- Close the unloading valves, including internal hydraulic valve and external manual valve on tank trucks.
- Close the vent valve on the shipping container.
- Depressurize and drain the unloading hose, then disconnect it carefully.
- Carefully depressurize and disconnect vapor return hose.
- Replace caps, plugs, and flanges removed for unloading. Secure equipment covers.
- Follow appropriate regulations for securing empty tank truck or rail car for shipment.
- Disconnect ground clamp, remove wheel chocks, "Connected" sign(s), and/or derails. Unlock railroad switches.

9.5 Unloading Tank Trucks with Pressure

It is not recommended to unload tank trucks with pressure. Your supplier should be contacted before this procedure is used due to the high risk of high velocity liquid leaks in the event of equipment failures and the environmental impact of such unloading practices.

10 Environmental Considerations

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 methacrylate esters 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. Spills must be promptly reported to appropriate authorities and cleaned up.

10.1 Waste Disposal

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

Methacrylate ester wastes need to be reviewed for proper classification and treatment under national regulations. MMA and ethyl methacrylate are classified as 'listed wastes' under the US Resource Conservation and Recovery Act [RCRA] which regulates the generation, transportation, handling, storage, treatment and disposal of hazardous wastes in the US. The waste identification numbers are: U162 for MMA U118 for EMA and D001 (ignitable) for n-BMA and i-BMA. 2-EHMA is not a RCRA hazardous waste. In the EU, wastes are classified according to EU Directive 91/689/EEC on Hazardous Waste. In the UK, methacrylate esters are classified as 'hazardous' under the UK Hazardous Waste Regulations, 2005. Hazardous wastes may include, but not limited to, process wastes containing methacrylate esters, methacrylate ester contaminated wastewater, soil, debris, and empty containers.

Diluted methacrylate esters degrade easily in a biological treatment plant and may be treated in an on-site industrial wastewater treatment plant if allowed by the facility's discharge permit. Liquid methacrylate esters may also be sent to local public treatment works with the local authority's knowledge and approval. Dispose of absorbents or polymeric material containing methacrylate esters, by incineration. Liquid wastes can be collected for incineration or burning as a fuel in an approved permitted facility in accordance with national regulatory requirements.

When disposing of laboratory wastes or retained samples, be certain to keep methacrylate esters separate from incompatible materials, such as peroxides, to prevent polymerization.

10.2 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.

Even though methacrylate esters are 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. Promptly notify responsible pollution control agencies if methacrylate esters are spilled or released into surface water or to a municipal sewer system. 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. Spills can be contained temporarily by stacking sand bags or similar absorbent material. Avoid run-off into storm sewers routed to public waters.

Various regulatory authorities have rules for reporting certain substances that may be spilled, released, used, or stored by facilities at certain quantities. It is important for facilities handling methacrylate esters to know and understand the local rules for release reporting and public information concerning hazardous chemicals in the community.

In the US, MMA and EMA have established CERCLA Reporting Quantities [RQ] of 1000 pounds when released or spilled into the environment. The National Response Center [NRC] must be notified in the event of a release or spill greater than 1000 pounds. MMA has been designated as a Superfund Amendments and Reauthorization Act (SARA) Title III Section 311/312 hazardous chemical requiring local community notifications. MMA is also a SARA Section 313 chemical requiring annual reporting of releases from point sources and fugitive emissions.

In the UK releases of methacrylate esters must be reported as per the Reporting of Injuries, Diseases and Dangerous Occurrences (RIDDOR) Regulations 1995. Other regulatory authorities have different requirements.

10.3 Air Emissions

Discharges into the atmosphere of gases containing certain chemicals are subject to restrictions in most countries. Air emissions must therefore be controlled and approved in accordance with applicable air emission control regulations. Some methacrylate esters are classified as Volatile Organic Compounds [VOC] under the US Clean Air Act. MMA is listed by the US EPA as a Hazardous Air Pollutant under the Clean Air Act Amendment of 1990. In the EU, the storage and use of methacrylate esters may fall under the Integrated Pollution Prevention and Control Directive (96/61/EC) and the REACH Regulation (EC No 1907/2006). Users must be responsible to ensure that their air emissions are in compliance.

Direct emissions to the atmosphere are to be controlled and permitted where necessary. Closed loop or vapor balancing unloading can be effective in reducing and controlling unloading emissions and odors. Closed loop unloading should be followed in storage, loading, and unloading facilities. However, there is a danger of contamination when vapor return lines are connected to a common vent header for multiple storage tanks. Methacrylate ester vapors are uninhibited and if these condense and collect in the vapor return system they may polymerize causing blockage. Systems should therefore be designed such that they drain back into the bulk of the product and do not contain dead legs where condensed vapor can collect.

Exhaust gases rich in methacrylate esters should be scrubbed before being released into the atmosphere. The exhaust gas can be incinerated in a flare if one is conveniently available. Catalytic incineration is a further option.

Methacrylate esters can be readily scrubbed with a sodium hydroxide and/or amine solution from vent gases. Depleted or spent scrubber solution can be drained into a biological treatment plant or incinerated, if permitted.

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

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