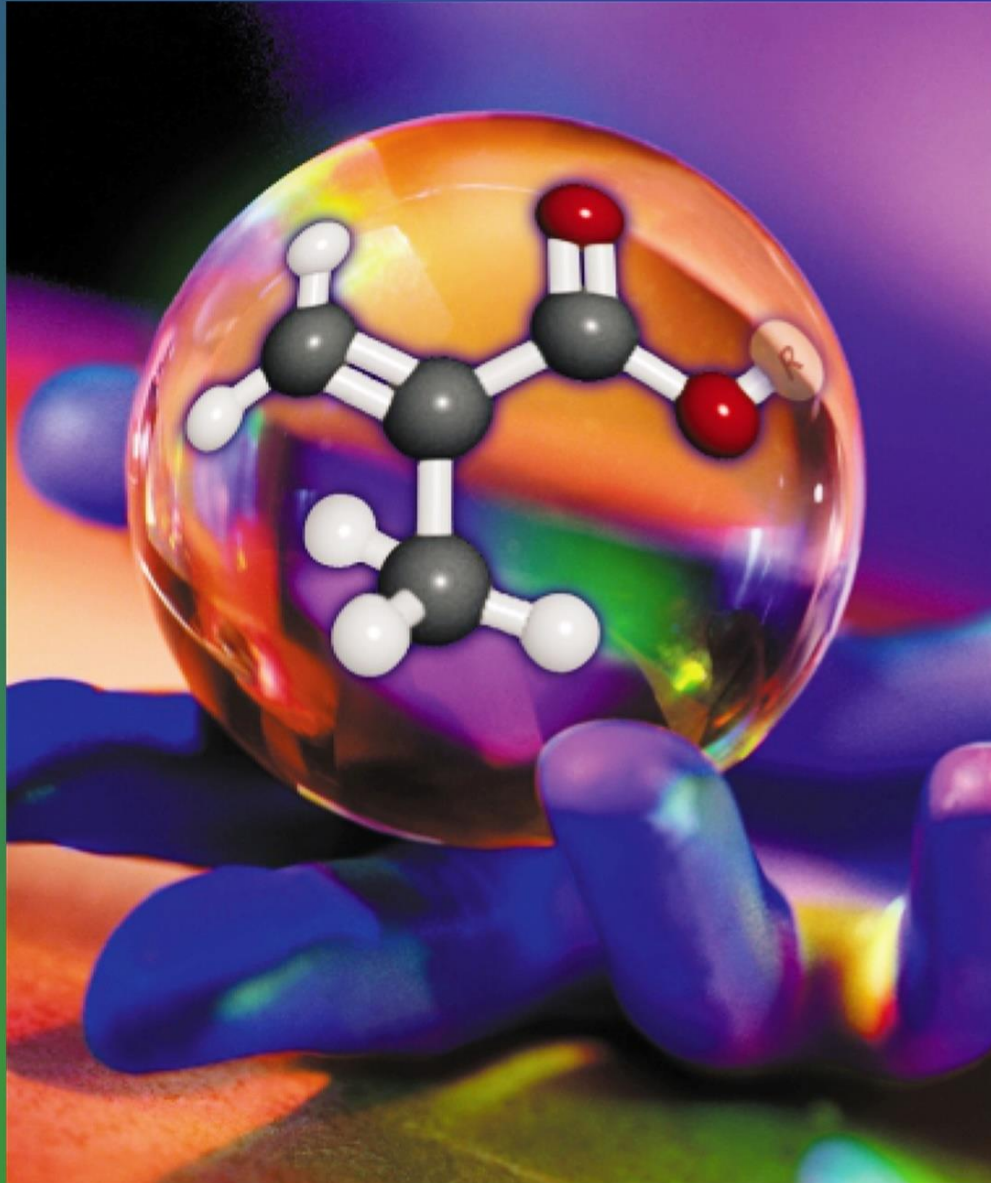


# METHACRYLATE ESTERS

## SAFE HANDLING MANUAL



Methacrylate Producers Association, Inc. and  
Methacrylates Sector Group of the European Chemical Industry Council

2019

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## INTRODUCTION

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This Manual provides general information on the safe handling of the lower molecular weight methacrylate esters: 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) as well as dealing with specific hazards in an appropriate manner. These hazards include health risks, environmental risks, flammability risks and the potential for uncontrolled polymerization.

The properties and characteristics provided in this Manual refer to methacrylate esters with a minimum purity of 98 percent. They conform to specifications reported in the technical information bulletins issued by methacrylate ester manufacturers but are provided for information purposes only. Since some of the physical data might be subject to minor changes due to differences in levels of impurities, refer to the technical specification and Safety Data Sheet ("SDS") produced by your supplier for product specific information.

The aim of this document is to bring attention to important safety and operational information for the use of methacrylate monomers. It is suggested that this information be included by the user in the formal assessment of hazards and risks for the user's specific situation.

**Please read this entire Manual before transporting, storing, or handling methacrylate esters or before designing a storage system for the esters. It is recommended that the preventive measures described in this Manual be followed to minimize the risks associated with these substances.**

## PREFACE

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**This Manual is a publication of the Methacrylate Producers Association, Inc. (MPA) and the Methacrylates Sector Group (MSG) of the European Chemical Industry Council (Cefic) and provides an overview of generally accepted practices for product stewardship for methacrylate esters. It provides general information for users of Methyl Methacrylate, Ethyl Methacrylate, n-Butyl Methacrylate, i-Butyl Methacrylate, and 2-Ethylhexyl Methacrylate about the hazards associated with handling these chemicals together with recommended measures to protect human health, equipment, and the environment. The principle hazards to be aware of include skin sensitization, flammability, and the potential for uncontrolled, rapid polymerization. Please read and familiarize yourself with this entire Manual before using the information it contains. Also, it is strongly recommended to thoroughly review your supplier's labels and Safety Data Sheets for methacrylate esters before working with them.**

Additional assessments and information on these chemicals are available on the European Chemicals Agency (ECHA) website and the Methacrylate Producers Association and Cefic Methacrylates Sector Group websites.

The information in this manual is current as of March 25, 2019 and was prepared by the following organizations:

**Methacrylate Producers Association, Inc. (MPA)**  
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[www.mpausa.org](http://www.mpausa.org)

**Methacrylates Sector Group of the European Chemical Industry Council (MSG)**  
Avenue van Nieuwenhuysse, 4-B 1, B-1160 Brussels, Belgium  
<http://www.petrochemistry.eu/about-petrochemistry/products.html>

**Although MPA and Cefic believe that the information contained in this Manual is factual, it is not intended as an assertion of legal requirements with respect to handling methacrylic esters. Consultation is required 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.**

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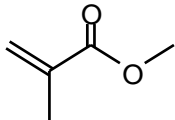
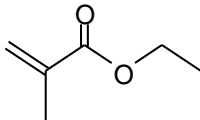
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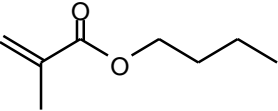
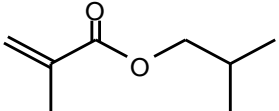
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# 1 CHEMICAL IDENTIFICATION DATA

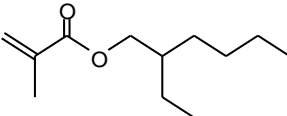
COMMON NAME	METHYL METHACRYLATE	ETHYL METHACRYLATE
CAS number	<b>80-62-6</b>	<b>97-63-2</b>
CAS name	2-Methyl-2-Propenoic Acid, Methyl Ester	2-Methyl-2-Propenoic Acid, Ethyl Ester
UN number	1247	2277
EEC number	607-035-00-6	607-071-00-2
Synonyms	MMA	EMA
	Methacrylic acid, Methyl Ester	Methacrylic acid, Ethyl Ester
	Methyl Methacrylate Monomer	Ethyl Methacrylate Monomer
	Methyl, 2-methyl-2-Propenoate	Ethyl, 2-methyl-2-Propenoate
EINECS number	201-297-1	202-597-5
Chemical formula		
Stoichiometric formula	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>
Hazard class and category code(s)	Flam. Liq. 2 Skin Irrit. 2 Skin Sens. 1 STOT SE 3	Flam. Liq. 2 Skin Irrit. 2  Skin Sens. 1 Eye Irrit. 2 STOT SE 3
Hazard statement code(s)	H225 H315 H317 H335	H225 H315 H317 H319 H335
Pictograms, signal word codes(s)	GHS02 GHS07 Dgr	GHS02 GHS07 Dgr
Specific Concentration limits, M-Factors		
Notes	Note A	Note A
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

**1 CHEMICAL IDENTIFICATION DATA (continued from previous page)**

<b>COMMON NAME</b>	<b>N-BUTYL METHACRYLATE</b>	<b>ISO-BUTYL METHACRYLATE</b>
CAS number	<b>97-88-1</b>	<b>97-86-9</b>
CAS name	2-Methyl-2-Propenoic Acid, n-Butyl Ester	2-Methyl-2-Propenoic Acid, i-Butyl Ester
UN number	2227	2283
EEC number	607-033-00-5	607-113-00-X
Synonyms	n-BMA	i-BMA
	Methacrylic acid, n-Butyl Ester	Methacrylic acid, i-Butyl Ester
	n-Butyl Methacrylate Monomer	Iso-Butyl Methacrylate Monomer
	n-Butyl, 2-methyl-2-Propenoate	Iso-Butyl, 2-methyl-2-Propenoate
EINECS number	202-615-1	202-613-0
Chemical formula		
Stoichiometric formula	$C_8H_{14}O_2$	$C_8H_{14}O_2$
Hazard class and category code(s)	Flam. Liq. 3 Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2STOT SE 3	Flam. Liq. 3 Skin Irrit. 2 Skin Sens. 1B STOT SE 3
Hazard statement code(s)	H226 H315 H317 H319 H335	H226 H315 H317 H335
Pictograms, signal word codes(s)	GHS02 GHS07 Wng	GHS02 GHS07 Wng
Specific Concentration limits, M-Factors		
Notes	Note A	Note A
IMDG	Class 3	Class 3
49 CFR, ICAO, IATA Packing Group	III	III
ICAO- CLASS	Class 3	Class 3
ADA/RID Orange plate	39/2227	39/2283
ADR/ RID Classification	Class 3	Class 3



**1 CHEMICAL IDENTIFICATION DATA (continued from previous page)**

<b>COMMON NAME</b>	<b>2-ETHYLHEXYL METHACRYLATE</b>
CAS number	<b>688-84-6</b>
CAS name	2-Methyl-2-Propenoic Acid, 2-Ethylhexyl Ester
UN number	1993
EEC number	607-134-00-4
Synonyms	2-EHMA
	Methacrylic acid, 2-Ethylhexyl Ester
	2-Ethylhexyl Methacrylate Monomer
	2-Ethylhexyl—2-methyl-2-Propenoate
EINECS number	211-708-6
Chemical formula	
Stoichiometric formula	C <sub>12</sub> H <sub>22</sub> O <sub>2</sub>
Hazard class and category code(s)	Skin Irrit. 2 Skin Sens. 1B Eye Irrit. 2STOT SE 3 Aquatic Chronic 3
Hazard statement code(s)	H315 H317 H319 H335 H412
Pictograms, signal word codes(s)	GHS07 Wng
Notes	Note A
IMDG	Not subject to dangerous goods regulations
49 CFR, ICAO, IATA Packing Group	Not subject to dangerous goods regulations
ICAO- CLASS	Not subject to dangerous goods regulations
ADA/RID Orange plate	Not applicable
ADR/ RID Classification	Not subject to dangerous goods regulations

**Note A: CLP Classification**

Substances which are susceptible to spontaneous polymerization or decomposition are generally placed on the market in a stabilized form. If placed on the market in a non-stabilized form the supplier must state on the label the name of the substance followed by the words ‘non-stabilized’

## 2 PROPERTIES OF METHACRYLATE ESTERS

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### 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 properties and characteristics provided in this Manual refer to methacrylate esters with a minimum purity of 98 percent. 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 differences in levels of concentrations of impurities.

The values in the following table were principally taken from the European Chemical Agency (ECHA) REACH Registration Dossiers unless otherwise specified. The information given is the most current as of April 1<sup>st</sup> 2019.

ECHA is an agency of the European Union which manages the technical, scientific and administrative aspects of the implementation of the European Union regulation called **Registration, Evaluation, Authorisation and Restriction of Chemicals**. ECHA is the driving force among regulatory authorities in implementing the EU's chemicals legislation. ECHA helps companies to comply with the legislation, advances the safe use of chemicals, provides information on chemicals and addresses chemicals of concern. For more information, see: <https://www.echa.europa.eu/web/guest/information-on-chemicals>.

## 2.2 SUMMARY OF PROPERTIES AND CHARACTERISTICS

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)	100.36 <sup>1</sup>	118-119 <sup>1</sup>	163 <sup>1</sup>	155 <sup>1</sup>	227.6 <sup>1</sup>
Freezing Point (°C)	-48	< -75 <sup>1</sup>	-50 <sup>1</sup>	-35 <sup>1</sup>	< -50 <sup>1</sup>
Density (g/cc at 20°C)	0.94 <sup>1</sup>	0.91 <sup>1</sup>	0.89 <sup>1</sup>	0.88 <sup>1</sup>	0.884 <sup>1</sup>
Refractive Index (at 20°C)	1.412	1.4115	1.4211	1.42	1.44 <sup>2</sup>
Viscosity (mPa-s or cP at 20°C)	0.53 <sup>1</sup>	0.56 <sup>2</sup>	1.04 <sup>2</sup>	1.00 <sup>2</sup>	2.65 <sup>2</sup>
Vapor Pressure (hPa at 20°C)	37 <sup>1</sup>	20 <sup>1</sup>	2.12 <sup>1</sup>	2.11 <sup>1</sup>	0.065 <sup>1</sup>
Flash Point, (Tag Closed Cup, °C)	10 <sup>1</sup>	18 <sup>1</sup>	48.5 <sup>1</sup>	42.5 <sup>1</sup>	97 <sup>1</sup>
Water Solubility (g/100g at 20°C)					
Monomer in water	1.53 <sup>1</sup>	0.469 <sup>1</sup>	0.036 (25°C) <sup>1</sup>	0.047 <sup>1</sup>	0.00031 <sup>1</sup>
Water in monomer	0.99 <sup>2</sup>	0.64 <sup>2</sup>	0.3 <sup>2</sup>	0.3 - 0.4 <sup>2</sup>	0.14 <sup>2</sup>
Explosive Limits (101kPa, 760mmHg)					
Lower	2.1 <sup>4</sup>	1.8 <sup>4</sup>	2 <sup>4</sup>	1	
Upper	12.5 <sup>4</sup>	saturation <sup>4</sup>	8 <sup>4</sup>	7.4	
Latent Heat of Vaporization					
KJ/Mole	39.5	40.6	50.0	47.2	
Kcal/Mole	9.4	9.7	11.9	11.3	
Heat of Polymerization (KJ/Mole)	54.0 <sup>5</sup>	59.1 <sup>2</sup>	56.6 <sup>2</sup>	59.9 <sup>2</sup>	
Specific Heat (20-30°C)					
KJ/Kg-°K	1.90	1.70	1.97	1.89	2.01 <sup>2</sup>
Cal/g-°C	0.45	0.41	0.47	0.45	0.48 <sup>2</sup>
Partition Coefficient					
Log Pow (Octanol/Water) 20°C	1.38 <sup>1</sup>	1.87 <sup>1</sup>	2.99 <sup>1</sup>	2.95 <sup>1</sup>	4.95 <sup>1</sup>
Henry's Law Constant (Pa-m <sup>3</sup> /mol)	22 - 33 <sup>3</sup>	34 - 62 <sup>3</sup>	50 - 55 <sup>3</sup>	47 - 52 <sup>3</sup>	
Autoflammability (°C)	435 <sup>1</sup>	400 <sup>1</sup>	294 <sup>1</sup>	385 <sup>1</sup>	250 <sup>1</sup>
Tg of Polymer (°C)	105 <sup>2</sup>	65 <sup>2</sup>	20 <sup>2</sup>	55 <sup>2</sup>	-10 <sup>2</sup>
Odor Threshold (ppm)	0.75 <sup>6</sup>	0.17 <sup>6</sup>	0.06 <sup>6</sup>	0.069 <sup>6</sup>	0.76 <sup>6</sup>
Self-Accelerating Polymerization Temperature (SAPT) (°C)	Greater than 55 °C	Greater than 55 °C	Greater than 55 °C	Greater than 55 °C	Greater than 55 °C

### References

1. ECHA REACH Registration Dossier Key Value
2. San Esters Corp. ([www.sanesters.com](http://www.sanesters.com))
3. Atmos. Chem. Phys., 15, 4399-4981, 2015
4. Sax's Dangerous Properties of Industrial Materials, 10<sup>th</sup> Edition, Wiley & Sons Inc. , 2000
5. Heats of Polymerization of Acrylic Acid and Derivatives, Evans and Tyrrell, Journal of Polymer Science, Vol 2, No 4, 1947
6. Dupont Odour Detection Panel Letter 1977

### 3 TRAINING AND JOB SAFETY

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The US Occupational Safety and Health Administration's (OSHA) Hazard Communication Standard (29 CFR § 1910.1200), and the EU Classification Packaging and Labeling of Dangerous Substances (CLP) Regulations (European Regulation (EC) No. 1272/2008, as amended) define what summary information is required to define and communicate the hazards posed by any chemical. This information is presented within the Safety Data Sheet (SDS) in a common format which conforms to the United Nations' Globally Harmonized System (GHS) on the classification and labeling of chemicals.

As set out in the regulations, it is the responsibility of an employer to use SDS information to provide its employees with adequate health and safety information and training to handle any chemicals used. For methacrylate esters this information is provided in your supplier's SDS, in this manual and other material generally available. The training requirements have been outlined in the Hazard Communication Standard and the EU Directive.

Before undertaking any training of employees who will be engaged in handling or processing methacrylate esters, it is recommended that the supervisor who will conduct the training be thoroughly familiar with the storage, handling, and properties of methacrylate esters together with any applicable national, state or local governmental occupational safety and health regulations. It is important to thoroughly review and understand your supplier's SDS and the information in this safe handling manual. If required, consult a safety specialist at your supplier before finalizing a safety review of your operations involving methacrylate esters.

#### References

- OSHA Hazard Communication Standard - <https://www.osha.gov/dsg/hazcom/>
- EU Classification Packaging and Labeling of Dangerous Substances Regulations - [https://ec.europa.eu/growth/sectors/chemicals/classification-labelling\\_en](https://ec.europa.eu/growth/sectors/chemicals/classification-labelling_en)
- Methacrylate Esters Safety Data Sheets

## 4 POTENTIAL HAZARDS

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When transporting, storing and using methacrylate esters the principal significant hazards to be aware of and manage safely are:

### 4.1 FIRE

The methacrylic esters covered by this manual (with the exception of 2-EHMA) are organic chemicals which are flammable, and therefore present the risk of ignition and fire.

### 4.2 POLYMERIZATION

Methacrylic esters polymerize exothermally. When this occurs, they present the risk of generating pressure and temperature. Methacrylic ester monomers are stabilized using polymerization inhibitor additives at a level appropriate to the anticipated storage temperatures and duration of storage. These stabilizers require the presence of oxygen to function, and thus oxygen availability is a key consideration in the storage of methacrylate monomers. Storage of methacrylate monomers with an inert gas atmosphere will prevent the stabilizers from functioning correctly; to avoid risk of dangerous polymerization, do not store methacrylate monomers with an inert gas atmosphere.

### 4.3 HEALTH

Direct contact with methacrylic esters liquid or vapor can cause irritation of human tissues. Personal protective equipment (PPE) may be mandated by workplace safety regulations and use of appropriate PPE when there is the potential for contact with these chemicals will minimize potential for adverse irritant effects.

Generally, work systems and practices are designed to limit the potential for personal exposure based on recommended guidelines and to comply with all regulatory requirements.

It is recommended that the information contained within this manual be incorporated in business and facility operational and emergency management assessments, procedures and training.

## 5 HEALTH MANAGEMENT

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For references on detailed health and safety evaluations of methacrylate esters, see Section 5.5.

### 5.1 TOXICITY

Methacrylate esters (MMA, n-BMA, i-BMA, EMA, and 2-EHMA) pose an acute hazard to health because the liquid and vapors can 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 a skin allergy, in which case 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, and may cause irritation of the mouth, throat, esophagus, and stomach.

Inhalation of high concentrations of vapors or mists of methacrylate esters can cause irritation of the respiratory tract and may cause dizziness and lightheadedness. 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 5.3 Industrial Hygiene for more information. Consult your supplier's current SDS for current toxicological information.

### 5.2 FIRST AID

Awareness of the need for prompt and appropriate response by all personnel assigned to work with methacrylate esters can minimize adverse consequences of methacrylate esters incidents. Technical data from the supplier and the SDS, in combination with information from this Manual, will assist in setting up an effective first aid program for methacrylate esters.

Many employers have, and regulations frequently require, installation of a sufficient number of conveniently located emergency safety showers and eye wash stations for a prompt response to methacrylate exposure incidents.

If possible, in light of the conditions at the scene and potential injuries, the first response after raising the alarm is the removal of anyone exposed to methacrylate esters from the immediate area to prevent further exposure. Then, the first responder can determine the type of exposure the person has experienced, e.g., eye or skin contact, inhalation or ingestion. If possible, do not leave an injured person alone. While immediate assistance is being provided to the affected individual, it may be necessary to obtain additional support including emergency services assistance.

If hospital treatment is required, ensuring that a copy of the SDS for the chemical causing the exposure is sent to the hospital with the worker will allow medical staff to more rapidly understand and define treatment requirements.

**The following recommended first aid instructions generally apply to contact with the eyes, inhalation, contact with skin, and ingestion, respectively, but please consult the SDS of the particular methacrylate ester for further information.**

### 5.2.1 Contact with the Eyes

Flush eyes with large amounts of lukewarm water for at least 15 minutes if a methacrylic ester comes in contact with the eyes. Hold the eyelids wide open and away from the eyeballs. The assistance of a helper is advised to make sure that all material is removed. Do not place oils or oily ointments or neutralizers in the eyes or on the eyelids unless ordered by professional medical staff. Obtain professional medical assistance.

The American College of Occupational and Environmental Medicine (ACOEM) provides guidelines for persons with contact lenses as follows: In the event of a chemical exposure, begin eye irrigation immediately and remove contact lenses as soon as practical. Do not delay irrigation while waiting for contact lens removal as the lens may come out with the irrigation or can be removed when irrigation is complete. Instruct workers who wear contact lenses to remove the lenses at the first signs of eye redness or irritation. Remove contact lenses only in a clean environment and after the worker has washed his or her hands.

### 5.2.2 Inhalation

Remove personnel affected by methacrylate esters vapors immediately to fresh air. If an individual is not breathing, administer artificial respiration and keep at rest. If symptoms develop or persist then seek professional medical assistance.

### 5.2.3 Contact with Skin

In the event of skin contact with a methacrylate ester, wash the exposed area immediately with water. In the event of significant exposure, use the nearest emergency safety shower. 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. Do not apply any salves or ointments unless prescribed by a physician.

All contaminated clothing will require decontamination before reuse. Where decontamination is not feasible, properly dispose of the clothing, including contaminated shoes and other leather items. To prevent exposure of any other persons to the methacrylate, do not take contaminated clothing for laundering.

### 5.2.4 Ingestion

If the methacrylate ester is swallowed, rinse the mouth. Do NOT induce vomiting. Get immediate medical attention.

### 5.3 INDUSTRIAL HYGIENE

Generally, exposure to methacrylate esters by inhalation, ingestion, or skin or eye contact can be prevented by a combination of engineering controls and good work practices. Engineering controls such as closed systems and local exhaust ventilation are the primary methods used, and are subject to national, state, and/or local governmental regulations. Workplace monitoring is recommended to determine typical exposure levels associated with the work tasks and to determine if additional control measures, e.g. engineering controls or personal protective equipment (PPE), are necessary. For airborne exposures, there are three types of limits in common use:

- the time-weighted average (TWA) exposure limit - the maximum average concentration of a chemical in air for a normal 8-hour working day and 40-hour week;
- the short-term exposure limit (STEL) - the maximum average concentration to which workers can be exposed for a short period (usually 15 minutes);
- the ceiling value - the concentration that should not be exceeded at any time

Effectiveness of engineering controls and other exposure controls can only be verified by workplace exposure measurements.

Although many of the higher molecular weight esters do not have exposure limits set at the present time, employers may decide to adopt an exposure limit similar to MMA for those esters. Occupational health standards-setting organizations in many countries have set workplace exposure limits for some of the methacrylate esters. Consult your supplier's SDS for the most current occupational standards for these compounds. Links to standards can also be found at the [International Labor Organization \(ILO\) website](#). Some typical examples of international occupational standards are given in the table below (as of January 2019):

Substance	Country	TWA or equivalent (8-hour)	STEL
MMA	Denmark	25 ppm	
	Norway	25 ppm	150 ppm
	Netherlands	50 ppm	100 ppm
	EU IOELV	50 ppm	100 ppm
	Germany	50 ppm	
	Sweden	50 ppm	100 ppm
	UK	50 ppm	100 ppm
	USA (ACGIH)	50 ppm	100 ppm
	USA (OSHA)	100 ppm	
	France	50 ppm	100 ppm
EMA	Denmark	25 ppm	
	Norway	50 ppm	
	Sweden	50 ppm	75 ppm
n-BMA	Denmark	25 ppm	
	Norway	10 ppm	
	Sweden	50 ppm	75 ppm
i-BMA	Denmark	25 ppm	
	Norway	50 ppm	
	Sweden	50 ppm	75 ppm



## 5.4 PERSONAL PROTECTIVE EQUIPMENT GUIDELINES (PPE)

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. Making the workplace safe includes providing instructions, procedures, training and supervision to encourage people to work safely and responsibly. However, even where engineering controls and safe systems of work have been implemented, some hazards might remain. PPE is equipment that will protect the user against those residual health or safety risks at work. It can include items such as safety helmets, gloves, eye protection, high-visibility clothing, safety footwear and safety harnesses. It also includes respiratory protective equipment (RPE).

The guidelines below are a starting point for developing your own PPE procedures. Generally, to develop such procedures, employers thoroughly assess the hazard of each task and select the most appropriate PPE. Employers generally provide, and often are required by regulations to provide, training in the correct use, care and limitations of PPE.

### 5.4.1 General recommendations

As a general guide the avoidance of inhalation of vapors and liquid contact with eyes and skin will protect against the potential adverse effects of methacrylate esters.

The PPE requirements for all tasks within a facility will be defined in that facility's operating standards and procedures. Compliance with those PPE requirements by all personnel in areas where methacrylate esters are handled will help to avoid incidents. As a general precaution, it is recommended that personnel in an area where there is the potential for exposure wear protective equipment, even if an individual is not planning to come in contact with the methacrylate esters.

Using anti-statically finished working garments and footwear is also recommended because of the flammable properties of these chemicals.

Commonly used hygiene measures include:

- No smoking or eating.
- Storage of work clothing separately.
- Immediate removal of soiled or soaked clothing.
- The usual good standards of occupational hygiene are followed.
- Thorough cleaning of skin after work.

### 5.4.2 Gloves

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, though it is noted 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. It is recommended that end users conduct suitability testing to determine most effective glove type and durability in their specific application.

Regular replacement of gloves, especially after known contact with the product, will help provide better protection by minimized the potential for breakthrough.

Suitable glove types will differ depending on need, as exposure differs with different tasks.

For more detailed safety information on gloves, refer to the '*Methacrylate Monomers: Safe Use of Gloves – Best Practice Guidance*' which is available on the MPA and CEFIC websites.

#### 5.4.3 Routine Work

It is recommended to carry out assessments to determine the most effective personal protective equipment required across the workplace. General considerations include the needs for routine, non-routine and emergency situations.

For personnel engaged in routine work with a small risk of limited exposure, such as collecting a sample or operating processing equipment, the following protective equipment might be a basic requirement: chemical-resistant gloves, safety shoes, and chemical splash goggles. Depending on the situation, consider wearing antistatic chemical-resistant boots if surface exposure might be anticipated.

Air-purifying respiratory protective equipment can protect against inhalation exposure, if air monitoring has demonstrated that airborne concentrations of methacrylate esters are above the applicable exposure limit and engineering controls are insufficient or unavailable to reduce such airborne concentrations.

#### 5.4.4 Non-Routine Work

For personnel engaged in non-routine work 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, the following protective equipment might be basic requirements: chemical-resistant suits, chemical-resistant boots and gloves, and chemical splash goggles. A face shield and/or chemical resistant hood can reduce potential exposure when opening drums or lines that may be under pressure.

Air-purifying respiratory protective equipment can protect against inhalation exposure, and is recommended if airborne concentrations of methacrylate esters above the applicable exposure limit might be expected. Respirator masks with a gas type filter meeting EN 14387 type A, 29 CFR 1910.134 - Respiratory Protection or equivalent requirements are generally the most effective to protect against exposure.

For higher vapor concentrations, a supplied-air respirator may be indicated and even required by an applicable regulatory program.

## 5.4.5 Emergencies

In events such as spills, vapor clouds or fire situations where there is a risk of exposure to airborne concentrations of methacrylate esters in excess of 100 ppm, then full protective PPE can prevent exposure and injury. This would typically include 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, evacuate the area immediately. If it is safe to do so, then isolate the supply of flammable material to the source of the leak. Properly trained personnel equipped with appropriate PPE for that situation can assist in safely addressing the situation. It is advisable to have several sets of PPE available at all times. Keeping this equipment well-maintained and stored outside of, but near, the area where the methacrylate esters are used will maximize its readiness.

To prevent the potential for serious injury, personnel should not enter areas with an airborne concentration level above the Lower Explosive Limit provided in Section 2.2. Evacuate the area immediately.

## 5.5 REFERENCE SOURCE MATERIAL ON METHACRYLATE ESTERS

### 5.5.1 OECD SIDS Initial Assessment Profile for Methacrylate Esters (2004)

<http://webnet.oecd.org/hpv/ui/handler.axd?id=941413ce-0b52-4c29-8002-baf3d8fd25fc>

### 5.5.2 ECHA Chemical Information

This is a unique source of information on chemicals manufactured and imported in Europe. It covers their hazardous properties, classification and labelling, and information on how to use them safely. See: <https://www.echa.europa.eu/web/guest/information-on-chemicals>.

Substance	CAS	Infocard	Registration Dossier
Methacrylic acid	79-41-4	<a href="https://echa.europa.eu/substance-information/-/substanceinfo/100.001.096">https://echa.europa.eu/substance-information/-/substanceinfo/100.001.096</a>	<a href="https://echa.europa.eu/registration-dossier/-/registered-dossier/15411">https://echa.europa.eu/registration-dossier/-/registered-dossier/15411</a>
Methyl Methacrylate	80-62-6	<a href="https://echa.europa.eu/substance-information/-/substanceinfo/100.001.180">https://echa.europa.eu/substance-information/-/substanceinfo/100.001.180</a>	<a href="https://echa.europa.eu/registration-dossier/-/registered-dossier/15528">https://echa.europa.eu/registration-dossier/-/registered-dossier/15528</a>
n-Butyl Methacrylate	97-88-1	<a href="https://echa.europa.eu/substance-information/-/substanceinfo/100.002.378">https://echa.europa.eu/substance-information/-/substanceinfo/100.002.378</a>	<a href="https://echa.europa.eu/registration-dossier/-/registered-dossier/15151">https://echa.europa.eu/registration-dossier/-/registered-dossier/15151</a>
Isobutyl Methacrylate	97-86-9	<a href="https://echa.europa.eu/substance-information/-/substanceinfo/100.002.376">https://echa.europa.eu/substance-information/-/substanceinfo/100.002.376</a>	<a href="https://echa.europa.eu/registration-dossier/-/registered-dossier/14969">https://echa.europa.eu/registration-dossier/-/registered-dossier/14969</a>
2-Ethylhexyl Methacrylate	688-84-6	<a href="https://echa.europa.eu/substance-information/-/substanceinfo/100.010.645">https://echa.europa.eu/substance-information/-/substanceinfo/100.010.645</a>	<a href="https://echa.europa.eu/registration-dossier/-/registered-dossier/14761">https://echa.europa.eu/registration-dossier/-/registered-dossier/14761</a>

## 6 FIRE HAZARDS

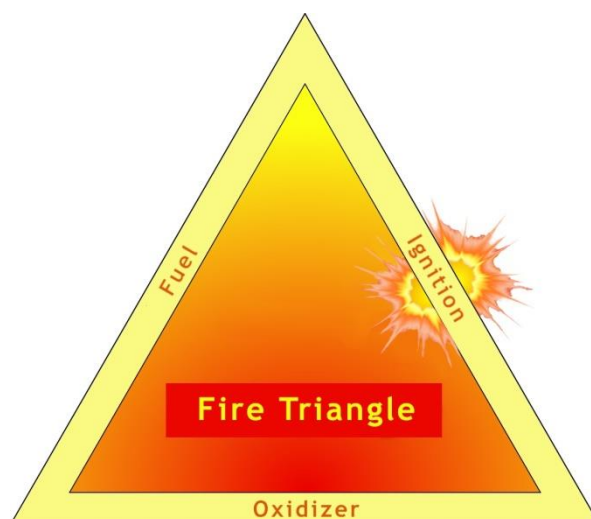
### 6.1 FLAMMABILITY

All methacrylate esters, with the exception of 2-EHMA, can form readily ignitable vapors at ambient temperatures. Methacrylate esters are typically handled at ambient temperature. The flash points and other flammability characteristics are listed in Section 2.2 and repeated below.

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
Boiling Point (°C at 101 kPa)	100.4	118	163	155	227
Flash Point, (Tag Closed Cup, °C)	10	18	48.5	42.5	97
Auto flammability (°C)	435	400	294	385	250
Vapor density	3.4	3.9	4.9	4.9	6.8

The three requirements for a fire to occur are the presence of:

- A fuel, in this case a methacrylate ester;
- An oxidizing agent, usually oxygen; and
- A source of ignition.



The storage and use of methacrylate esters have the potential for flammable vapors to develop. As indicated earlier, the polymerization inhibitors added to methacrylate esters require the presence of oxygen to function. Therefore, control of any fire risk from methacrylate esters generally focuses on the other two elements of the fire triangle, i.e., containment and control of ignition sources and avoiding creation of fuel (e.g., avoiding leaks and controlling vapors).

A minimum oxygen level of 5% is required to support the polymerization inhibitor functionality. If necessary, under appropriately engineered controls, it is possible to reduce storage oxygen levels to the 5% to 8% range. This will keep the vapor space outside of the flammability range while ensuring inhibitors can still function.

Methacrylate ester vapors are heavier than air and may travel a considerable distance to a source of ignition and flash back. Ignition may also occur if excessive amounts of mist or aerosol have formed in the air. Containers may fail in an external fire or when heated because of pressure build up due to boiling or polymerization releasing the contents.

Ignition sources can originate from many potential sources such as electrical equipment, spark discharges from static electricity, impact sparks, vehicles, lightning and many others. Hazardous area assessments to identify potential sources of ignition and employment of a combination of design measures and systems of work to control them can significantly reduce the risk of fire.

## 6.2 FIRE PREVENTION MEASURES

A flammable atmosphere likely exists internally in all storage containers and pipework, as well as externally in the event of any loss of containment. As previously stated, oxygen is required for the polymerization inhibitor to function, so **nitrogen blanketing of a vapor space to avoid fires would result in a serious hazard**. The key fire prevention measure is ensuring there are no sources of ignition in any area where this may be expected.

### Examples of the main causes of ignition are:

- **Static electricity** - The movement of fluids and rotating equipment can lead to the development of electrostatic charges commonly known as static electricity. These charges can be generated during the handling of methacrylate esters, but the proper bonding and earthing or grounding of equipment allows these to be dissipated. Without these precautions there is the potential for ignition.
- **Electrical equipment** - Electricity can provide a suitable spark to ignite methacrylate vapors. Periodically reviewed electrical zoning assessment can help ensure that all equipment installed in the facility has the right specifications to match the potential fire risk and regulatory requirement.
- **Lightning**- Effective lightning protection in storage facilities reduces the risk of lightning ignition and may be required under applicable regulations.
- **Maintenance** - During maintenance or construction activities new ignition sources may be introduced or existing protective systems deactivated. An assessment of potential fire risk in the planning and execution of these activities can help reduce the risk of ignition.
- **Measures to prevent sources of ignition** - It is recommended that expert guidance be sought to ensure that all engineering and operational best practice and regulatory requirements are properly implemented and maintained.

Examples of good practice general principles are:

- Be aware of all legislation pertaining to the storage and handling of flammable organic liquids in the design and operation of facilities.
- All containers and all interconnections such as hoses and fittings are electrically interconnected (bonded) and properly earth grounded.
- Use a dip tube rather than splash filling a tank which helps avoid static charges. If mixing nozzles are used in storage tanks, a minimum storage level of 500 mm (20 inches) above the nozzle outlet avoids spraying that can generate static charge. Statically ground dip pipes.
- At the start of transfer use lower flow velocities to minimize the formation of mists and aerosols. Once the end of the fill line is submerged then flow velocities may be increased. As a guide keep initial flow rates below 1 m/s then increase to around 2 to 3 m/s. Flammable solvents industry guidelines suggest that flow rates be kept below 7 m/s.
- The low flash points of the lighter methacrylate esters require that all permanent storage tanks be fitted with the legally obligatory fire protection equipment. In addition to reduce ignition risks, normal vent outlets into the atmosphere may require flame arrestors and consider using detonation traps for manifolded vents, particularly if the vent is connected to an ignition source such as a thermal oxidizer or flare. Flame arrestors may become blocked due to condensed monomer polymerization; regular inspection helps prevent blockage.
- Avoid cutting, drilling, grinding, or welding on or near drums and IBC as this can generate heat or electrical charges which could ignite residual material in these containers. Residual vapors in drums or containers may explode on ignition. Improper disposal or reuse of drums and IBCs may be both dangerous and illegal. Ensure that drums are treated such that any hazards are appropriate for the disposal route used.
- Prohibit smoking in the workplace.

### **6.3 FIRE EMERGENCY RESPONSE PLANNING**

The information contained in this manual together with local requirements can be used to develop a site Fire Emergency Response Plan. A fire emergency management plan details your arrangements to implement, control, monitor and review fire safety standards and to ensure those standards are maintained. The plan describes the arrangements for effectively managing fire safety so as to prevent fire occurring and, in the event of fire, to protect people and property. The basis for the response plan is a formal fire safety risk assessment. Some observations on methacrylate ester properties pertinent to fire emergencies are:

- To assess what will be the most risk-free locations to respond to any situation, firefighting personnel can consider that 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, spraying tanks and pipes with plenty of water may cool the monomers and prevent them from polymerizing. It is also recommended to assess whether short stopping agents can be safely added to tanks as part of the fire emergency plan.

- Keeping any drums or containers cool with water spray while personnel are fighting the fire can prevent the explosive rupture of sealed containers and potential ignition of vapors emitted. Effective fire extinguishing agents include dry chemical, foam, and carbon dioxide. Medium expansion foams are particularly effective for pool fires that can result from storage loss of containment.
- 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. Adding short stopping agent to the collection of spilled materials, as these may now be contaminated, helps prevent polymerization.
- Regional, country, state or local authorities may require you to plan for the containment of runoff of firefighting materials.

See Section 5.4 for Personal Protective Equipment information.

## 7 INSTABILITY AND REACTIVITY HAZARDS

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### 7.1 POLYMERIZATION RISK

**Methacrylate esters are highly reactive. Polymerization of methacrylate esters can be energetic, with reactions producing considerable heat and pressure with the potential to eject hot polymer and monomer from the site of polymerization if containment is lost.**

Generally, the lower molecular weight esters are more hazardous than those with higher molecular weight. However, contamination can affect the rate of reaction such that even a higher molecular weight monomer can react quickly and violently.

In the event of polymerization a fire or over pressure hazard may exist because of rapid pressure build-up of hot flammable vapors, especially if the material is in a closed or poorly vented container. A runaway methacrylate ester polymerization reaction will generate temperatures well in excess of the monomer boiling point. There is no guaranteed or warranted method for relieving the pressure from such a runaway with the consequent potential for rupture of the tank or container.

Typically, methacrylate esters contain stabilizer levels that provide a shelf life of six months or more at local ambient conditions. Exceptions do exist; your supplier can provide information for the specific monomer and grade purchased. Maintaining awareness of shelf life requirements and meeting them can help avoid hazards.

## 7.2 STABILIZATION USING POLYMERIZATION INHIBITORS

Commercially available methacrylate esters are stabilized by a combination of dissolved oxygen and polymerization inhibitors to prolong shelf life. Polymerization inhibitors include:

Stabilizer	Common names	CAS number	Other names and trade names
Mono methyl ether of hydroquinone	MEHQ	150-76-5	para-methoxyphenol (PMP) and 4-Hydroxyanisole (HA)
Hydroquinone	HQ	123-31-9	
2,4-Dimethyl-6-tert-butylphenol	Topanol-A®, AO30®	1879-09-0	BDMP, DMTBP, IONOL K78®, 6-(tert-Butyl)-2,4-xlenol
2,6,-Di-tert-butyl-4-methylphenol	Topanol-O®	128-37-0	BHT
<ul style="list-style-type: none"> <li>• These stabilizers may also be known by alternative trade names.</li> <li>• The addition level of a stabilizer will be determined by the supplier to meet product shelf life requirements. The rate of depletion of a stabilizer is a function of temperature and time.</li> <li>• All stabilizers require the presence of oxygen to function, and storage or handling under an inert atmosphere will prevent stabilizers from functioning causing a risk of polymerization. <b>Never store or handle methacrylate esters under an inert atmosphere.</b> Sufficient concentrations of dissolved oxygen in the monomer can be achieved by maintaining a vapor space containing air or mixed gas containing at least 5% oxygen above the monomer.</li> </ul>			

## 7.3 CAUSES OF UNINTENDED POLYMERIZATION

There are five main causes of unintended polymerization of methacrylate esters:

- **high temperatures leading to inhibitor depletion;**
- **contamination initiating reaction;**
- **lack of oxygen preventing stabilization;**
- **inhibitor depletion after long storage duration;**
- **corrosion products acting as reaction initiators.**

Care is required to manage these factors in storage and use to prevent unintended polymerization.

### 7.3.1 Effect of elevated temperatures

Commercially available methacrylate esters are inhibited with stabilizers which inhibit polymerization to provide a usable shelf life. A stabilizer reacts with free radicals that would otherwise cause polymerization. Over an extended period, the stabilizer is slowly consumed until eventually, when all the stabilizer has been used up, polymerization will occur. **Increasing temperature increases the rate of free radical generation, and therefore stabilizer consumption, and so reduces shelf life.** Avoiding storage at elevated temperatures and maintaining the temperature of methacrylate esters below 40°C (104°F) will help prevent the loss of stabilizer. Lower temperatures will extend the shelf life of the stabilizer.



Once the inhibitor has been used up, any free radicals then generated will be available to initiate polymerization. Once the stabilizer has been depleted, the addition of more stabilizer does not regenerate the storage life of the monomer because peroxide concentration will be high as a result of the free radical/inhibition process. These peroxides break down to generate new free radicals which can initiate polymerization. Therefore, the best way to ensure full shelf life of the delivered monomer is to properly manage storage conditions.

Some notes regarding elevated temperature:

- Stabilizer levels are generally specified by the supplier to maintain product stability within the recommended maximum shelf life (maximum storage time) at normal ambient temperatures encountered at a location.
- Higher temperatures may lead to a higher consumption rate of the stabilizer system and consequently to shorter shelf life and potentially an unintended polymerization.
- If stabilizer levels have been depleted due to time or temperature, then the addition of more stabilizer will not fully restore the shelf life to that of fresh monomer. The extension of storage life by the addition of extra stabilizer is not a recommended practice.
- Store methacrylate ester drums in the shade rather than the sun to help prevent high temperatures which reduce shelf life and increase the risk of unintended polymerization.
- Do not store in locations where the storage container may adsorb heat from other local equipment at higher temperature, such as for example steam pipes.

### 7.3.2 Contamination

By using well-designed facilities, proper handling procedures, and good housekeeping practices, contamination of stored methacrylate esters can be avoided. Many compounds are known to promote polymerization, for example: peroxides, compounds which form peroxides, and free radicals, including aldehydes, ethers, amines, azides, sulfuric acid and nitric acid. Ensuring that all containers and transfer lines are cleaned and free from other chemicals before they are used to transfer and store methacrylate esters helps prevent contamination.

Additionally, polymerizing methacrylate esters, which can be in localized or hot stagnant areas such as deadheaded pumps and heated transfer lines, can also contaminate monomer.

### 7.3.3 Stabilizer Depletion

Polymerization stabilizers added to inhibit polymerization are depleted with time. Elevated temperatures accelerate the rate of depletion. Observing the recommended storage time and temperatures helps prevent depletion of the inhibitor.

A separate water phase in storage tanks can develop over time. Some polymerization inhibitors used are soluble in water, and therefore tend to transfer out of the monomer phase and into the aqueous phase. This process reduces the level of stabilizer in the monomer phase and may significantly impair shelf life, increasing the likelihood of unintended polymerization. Monitoring for and avoiding a water phase reduces this risk.

#### 7.3.4 Stabilizer Deactivation through Oxygen Depletion

**Never store, transport or handle methacrylate esters under an oxygen-free atmosphere.**

**The presence of a sufficiently high level of dissolved oxygen in the monomer is essential for the effectiveness of the stabilizers that are added to monomers.** Storage, transportation and handling of methacrylate esters in an oxygen-free atmosphere will inhibit functioning of the stabilizer and present a hazard.

Because some of the methacrylate esters can vaporize sufficiently at ambient temperatures to form flammable mixtures, a nitrogen/oxygen gas mixture with less than 21% by volume of oxygen to avoid flammability is sometimes considered. Stabilizer effectiveness can be maintained by ensuring that the atmosphere above the monomer always contains more than 5% oxygen. Flammability hazards can further be reduced by using equipment designed and operated for the handling and storage of methacrylate monomers in flammable atmospheres.

**Maintaining a nitrogen/oxygen gas mixture containing 5-21% by volume of oxygen at one atmosphere in the vapor space above the monomer is necessary to ensure inhibitor effectiveness.**

**Maintaining a vapor space over the liquid of 5-10% of tank volume helps ensure oxygen is available for polymerization inhibition.**

Methacrylate esters will absorb water during storage, so it is recommended that a dry gas system is used.

Oxygen is consumed slowly as part of the free radical scavenging mechanism used to inhibit polymerization. Replenishing the atmosphere above methacrylate esters in a closed system such as drums with an air or nitrogen/ oxygen gas mixture of 5-21% by volume of oxygen prevents oxygen depletion, especially if the methacrylate ester is stored at higher ambient temperatures or is near the end of its recommended shelf life.

The vapor space over larger vessels open to the atmosphere will maintain the oxygen content by natural in-breathing. If the oxygen in the vapor space is reduced, consider introducing a gas sparge to maintain the monomer oxygen concentration. Do not use nitrogen as a purge gas in any level measurement system or for pressure transfer as it will eliminate oxygen and thus pose a risk of polymerization.

Self-draining lines or blowing out using a 5-21% oxygen-containing gas mixture can be used to remove residual amounts of monomers left in transfer lines and other stagnant areas. Do not blow transfer lines with nitrogen as it will eliminate oxygen and thus pose a risk of polymerization.

#### 7.3.5 Corrosion

Corrosion can pose a polymerization hazard. Under some circumstances, aqueous solutions of transition metal ions produced by corrosion can initiate polymerization. Metal ions result if there is corrosion in the storage or transportation system caused by:

- Presence of a water layer in a carbon steel tank;
- Contamination of the methacrylate esters with materials such as acids, which are corrosive to normal storage or piping systems.

## 7.4 POLYMERIZATION DETECTION

Methacrylate esters have the potential to polymerize rapidly, generating a large amount of heat. This can occur because the heat released on polymerization increases the system temperature and this then drives an increasing rate of reaction. **As a result, any temperature rise that cannot be related to an external heat source is most likely an indication of polymerization occurring.** Thus, monitoring the temperature carefully if an increase in storage temperature is noted that is not related to ambient conditions will inform appropriate safety measures. Even slow temperature rise can lead to a runaway polymerization event, such that corrective measures are warranted.

The rate of reduction of the polymerization inhibitors used with methacrylate esters increases as the storage temperature rises. The rate of loss of inhibitors can be reduced using storage facilities designed to minimize external heating effects due to ambient temperatures, solar gain or other heat sources.

**Simple test for low levels of polymer in monomer** - If a sample can be safely acquired, it can be used to test for the presence of soluble polymer to confirm polymerization has started. To test for polymer in the monomer, add 10 ml of the monomer to 90 ml of methanol or petroleum ether. The polymer is insoluble in the methanol or petroleum ether and this will result in the mixture becoming cloudy if there is any polymer present.

- **Key temperature action trigger points for bulk storage** - Temperature monitoring is employed to identify, investigate and address any sustained increases in storage temperatures. The following are, generally, key temperature triggers for management action:
- **Storage temperature rises to 45°C** - If the bulk temperature exceeds 45°C (113°F) without any obvious external heat source, then it is highly likely polymerization is occurring and corrective action is needed.
- **Rate of rise in storage temperature reaches 2°C per hour** - If the rate of temperature rise exceeds 2°C per hour then it is highly likely that polymerization is occurring and corrective action is needed.
- **Rate of rise in storage temperature reaches 5°C per hour** - If the rate of increase in storage temperature continues to rise and reaches 5°C per hour then an uncontrolled polymerization is occurring. Further increases in temperature will most likely occur, leading to further polymerization and the generation of significant quantities of flammable vapors and potentially a rise in internal pressure. Withdraw all personnel from the area and establish a security perimeter at a suitable distance.

If not already carried out adding short stopping inhibitor to the storage tank at this stage will help to arrest uncontrolled polymerization.

See Section 8: Response to Uncontrolled Polymerization for more information.

## SUMMARY:

- **Even slow polymerization has the potential to later 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) per hour and no source of external heat has been identified then it is highly likely that polymerization is occurring and action is needed.**
- **If the temperature rises at a rate greater than 5°C (9°F) per hour then the situation is critical.**

## 8 RESPONSE TO UNCONTROLLED POLYMERIZATION

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### 8.1 INTRODUCTION

The information below is intended to be used to assist in development of local Emergency Response Procedures. This section alone is not intended to serve as an Emergency Response Procedure.

The main potential reasons that an unintended polymerization occurring in storage would be:

- **Storage exceeds the recommended shelf life** - The manufacturer supplies monomers stabilized to meet the shelf life recommendations for the anticipated local climatic conditions. The stabilizer available will reduce over time, so if the monomer is stored for longer than the recommended shelf life the conditions to allow polymerization may occur.
- **Elevated temperature - Maintenance of the temperature of stored methacrylate esters below 40°C (104°F) avoids depletion of the inhibitor, and it is preferable to store well below this temperature. If local ambient temperatures exceed these conditions, then extra vigilance and the provision of methods for mitigating heat absorption will be warranted to avoid inhibitor depletion and polymerization risk.**
- **Lack of oxygen** - Polymerization inhibitors used with methacrylate monomers only function in the presence of oxygen. A safe storage condition for the vapor space over the monomer is the presence of oxygen content between 5% and 21%.
- **Introduction of a contaminant** - Good equipment design and operating procedures can reduce the likelihood of contamination. Poor housekeeping and lack of cleaning may result in contaminants entering the storage, which could then act as polymerization initiators. Maintaining good control over potential contamination helps prevent polymerization. If it is known or suspected that reactive contamination has occurred, then it may be prudent to assume that polymerization may occur, and appropriate management response may be needed.

## 8.2 TEMPERATURE MONITORING

While the potential for uncontrolled polymerization is low if precautions outlined here are followed, routine monitoring of the temperature of all stored methacrylate esters will help to ensure any uncontrolled polymerization is detected so that it can be appropriately addressed. The rate of temperature rise is the key indicator that polymerization may be occurring. Additional monitoring and management responses may be needed when any increase in temperature which cannot be attributed to environmental factors is observed.

**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, it is highly likely that polymerization is occurring and that action is needed.**

**If the temperature is above 55°C (131°F) or is rising at a rate greater than 5°C per hour then an uncontrolled polymerization almost certainly is occurring.**

Do not approach any tank or container of polymerizing methacrylate esters without prior emergency planning. **Never approach a container of uncontrolled polymerizing methacrylate esters if the rate of temperature rise has exceeded 5°C per hour (9°F per hour) with no external heat source. Consider this information in all management response choices.**

## 8.3 INITIAL MANAGEMENT RESPONSES

Once it has been determined that an uncontrolled polymerization may be occurring, emergency management control over the area, including evacuation if necessary, can reduce the risk of injury. Safe evacuation distances depend upon many factors, including the rate of polymerization, the likelihood and expected nature of potential loss of containment, and equipment design (size, vent area, design pressure, etc.) and other local factors. Risk can be minimized by planning these responses in advance and including appropriate actions as part of local Emergency Procedures. Your supplier can provide further advice in the development of your Emergency Response Procedures.

If the temperature continues to rise, consider applying cooling water to the exterior of the vessel to reduce the temperature of the methacrylate esters. The local emergency response team may 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. It is recommended that external water cooling is applied before the tank content temperature rises too much, as the effect of the sudden cooling effect may cause a rapid condensation of monomer vapor and result in an internal pressure reduction outside of tank relief and construction specifications causing the tank to lose integrity. Taking appropriate caution with fire water use can minimize impairment of the effectiveness of tank bunding and containment.

If it is determined that it is safe to approach the vessel, further risk can be reduced by ensuring adequate venting, which can occur by opening any closed top hatches, especially for tank trucks or rail cars.

**Caution: Do NOT attempt this if the temperature is already greater than 55°C, if a local pressure gauge indicates that the vessel is above atmospheric pressure, or if the vessel is venting flammable vapors.**

If it is suspected that a polymerization is occurring in a bulk storage tank then the addition of a short stopping agent can reduce risk by preventing further polymerization.

If a short stopping agent is not available, then risk can be reduced by continuing to apply external cooling, if it is safe to do so. Risk of injury can be reduced by establishing an effective emergency management perimeter, evacuating all non-essential personnel, and ensuring that all potential ignition sources have been isolated.

**UNDER NO CIRCUMSTANCES SHOULD ANYONE NOT TRAINED IN THE APPROPRIATE EMERGENCY RESPONSE TECHNIQUES APPROACH A TANK WHERE POLYMERIZATION IS THOUGHT TO BE OCCURRING.**

**A vessel undergoing an uncontrolled polymerization may experience high enough temperature to cause venting through pressure relief systems.**

**Vessel pressure relief systems are normally sized based on an external fire basis. In the event of a major polymerization event the rate of pressure rise or the presence of two phase viscous flow may result in the relief system not being capable of reducing internal pressure.**

**A polymerizing vessel that stops venting may have a plugged vent. The potential for a violent vessel rupture may then 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.**

## **8.4 SHORT STOPPING AND RESTABILIZATION**

The most effective response to an uncontrolled polymerization of methacrylate esters is the remote addition and mixing of shortstop inhibitor. Temperatures reached during a runaway polymerization will defeat the functionality of MEHQ, HQ or AO30 stabilizers and so these will not have any significant impact if added to a runaway polymerization of methacrylate esters.

Successful short stopping and destabilization of methacrylate esters in these circumstances requires a timely response to detection of a significant temperature increase. The lack of this response may result in the onset of uncontrolled polymerization leading to accelerated temperature and pressure rises with potentially significant consequences to the storage vessel. To be effective, short stopping agents need to be added to the vessel while the monomer contents are still mobile and not viscous.

### **8.4.1 Short stopping chemicals**

Phenothiazine (PTZ), CAS Number is 94-84-2, is the most widely recommended shortstop agent. PTZ is also known as Thiodiphenylamine, Dibenzothiazine, Dibenzoparathiazine and 10*H*-dibenzo-*[b,e]*-1,4-thiazine.

While PTZ often is the most effective option, it will not be effective in short stopping in every situation. If the addition is performed too late into an uncontrolled polymerization process, or if the polymerization is a result of significant over-addition of an initiator, then short stopping is unlikely to be effective. Short stopping works best when added as early into the reaction as possible.

#### 8.4.2 Short stop inhibitor solvents and concentrations

PTZ is a solid. Dissolving it in a suitable solvent before addition helps to distribute the PTZ evenly through the methacrylate ester. Examples of solvents used for shortstop PTZ are ethyl acetate, isopropyl acetate, N-methylpyrrolidone and tripropylene glycol. PTZ solutions are commercially available; examples are Allesan® Protacryl B15 and RESTAB.

Preparing the PTZ shortstop solution as highly concentrated as possible to minimize its volume allows it to be delivered by pressurized gas or pumped into the system in as short a time as possible. **The final concentration of PTZ in the methacrylic ester to be shortstopped may be in the range of 200 to 1000 ppm.**

In the case of contamination, depending on the nature and concentration of the contaminant, restabilization may not be possible at any concentration of PTZ.

#### 8.4.3 Short stopping agent addition

The capability for the addition of a short stopping agent generally is a part of the assessments performed as a part of setting up the storage facility for methacrylate esters. Two addition options are possible:

- **Pumped addition** - With this option, the PTZ solution would be held in an external tank adjacent to the storage facility. This tank is linked to a recirculation pump for the storage tank. Rapid mixing of the shortstop inhibitor solution with the methacrylate esters in the storage tank is achieved by eductor tubes located at the discharge of the acrylate tank pump circulation loop within the tank.
- **Pressurized gas addition** -The PTZ solution is held in a tank which is then pressurized by an air/nitrogen mixture when required. The PTZ is then injected under gas pressure into the storage tank using a suitably designed injection nozzle. Such systems are commercially available. PTZ does not depend on the presence of oxygen so nitrogen can be used in this situation to drive the transfer.

#### 8.4.4 Criteria for implementing the use of a short stopping addition

It is recommended that the short stop system be immediately activated if any of the following criteria are satisfied:

- A temperature rise of greater than 5°C per hour has been detected without external cause.
- The temperature in the liquid has reached 45°C without external cause.
- There is a fire near the methacrylic ester tank.
- A known polymerization initiator or incompatible substance has been added to the methacrylic ester.
- Any other evidence or knowledge that a polymerization has begun.

These criteria have been chosen to ensure adequate time for the restabilizing agent to be fed to and dispersed in the tank contents.

Any temperature or temperature rise that exceeds the possible rise from external heat sources (ambient, sun, pumps, temperature control systems, addition of warmer product, etc.), may indicate an on-going polymerization. Including temperature monitoring as a part of routine management systems will help to establish an understanding of normal temperature variations and to ensure that any uncontrolled polymerization is promptly detected. Based on an understanding of normal temperature variations, warning temperatures can be set and monitored for any deviations away from normal variation. Early identification of a reaction is essential to safety, and this most likely to be achieved if good management systems are in place. While the probability of unintended polymerization is very low under normal circumstances, polymerization is a potentially high consequence event, so proper awareness and effective management procedures are considered essential to maximize safe storage, handling and use of methacrylate esters.

## **9 TRANSPORTATION AND OFFLOADING**

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### **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. All employees involved in the shipping, receiving and unloading hazardous materials are normally required to be trained in the proper application of these regulations and safe handling guidelines.

Methacrylate esters require an oxygen containing atmosphere to maintain inhibitor activity, but the use of pure oxygen or any inert gas for sparging, blowing lines, or blanketing can be hazardous. Pure oxygen lowers the flash point, thus increasing flammability. Inert gases can reduce dissolved oxygen sufficiently to inactivate inhibitor and cause polymerization. When handling and storing methacrylate esters, air or a gas mixture of 5 to 21% by volume oxygen will help to reduce flammability without preventing proper functioning of inhibitors.

Cleanliness of the transport vessels is essential to prevent contamination that can cause polymerization. Certifying rail cars, trucks and isotanks as cleaned and dried and free of polymer before (re)use helps avoid contamination. Similarly, confirming that all storage tanks and containers and associated piping and equipment are free of contamination and any prior contents before loading can avoid potential polymerization of the entire contents.

Maintenance of a vapor space in tanks, containers and drums is typically required by shipping regulations and is necessary to provide oxygen to maintain inhibition.

Any retained samples can be safely stored in a cool, dark place for one year or less. Amber glass bottles reduce UV-initiated polymerization and are recommended for storing small amounts of methacrylate esters.

Particular care is recommended when removing protective caps on discharge pipes 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 as required by regulation or appropriate precaution. This would be for example:

- UK National Chemical Emergency Centre,
- CANUTEC (Canadian Transport Emergency Centre operated by Transport Canada or
- CHEMTREC (CHEMical TRansportation Emergency Center).

If a shipment in a railcar, tank truck, drum, or intermediate bulk container (IBC or tote) becomes damaged in transit so that delivery cannot be made safely, moving the container away from people and property as much as possible can prevent injury. Additionally, notifying the emergency services and restricting access to the area can further reduce the risks arising out of an incident.

## 9.3 SITE UNLOADING FACILITIES

The following are generally considered appropriate safety practices for unloading facilities:

- Establishment of facility procedures and operations that allow for the prompt detection of and response to abnormal events.
- Continuous monitoring of unloading until completed.
- Unloading during daylight. When it is necessary to unload at night then adequate lighting in the working areas helps ensure good visibility and full control over unloading hazards.
- Designing and arranging the unloading area so that the truck is driven into and off the pad in a forward direction without having to reverse into position.
- Use of a closed loop (vapor balanced) system to control odors and flammable vapors of methacrylate esters. Displaced receiving tank vapors are either returned to the tank truck or directed to vapor control equipment such as scrubbers, thermal oxidizers, or flares. Appropriate sizing of these systems can prevent over-pressure in the site tank and under-pressure in the delivering vehicle. The use of tanker pressure/vacuum valves as pressure relief during unloading poses a risk and is not recommended.

Equipment can be designed according to recommended practices for safe handling of flammable and polymerizable chemicals. General points of note include:

- Designing unloading areas to meet all legal requirements for handling flammable chemicals.
- Providing suitable stairs and access platforms for the unloading area. Consider whether fall arresting systems are warranted.
- Counter balancing of overhead unloading hoses or arms to avoid lifting injuries.
- Earth grounding with a positive indication of effective earthing being achieved during unloading, to help prevent ignition due to static discharge.
- Arranging unloading piping so that the material drains toward the storage tank when transfer stops.

- Using dedicated unloading hoses and storing effectively to avoid contamination. Where a hauler's hose is used, rinsing the hose with water allows for safe removal of product residues prior to leaving the site.
- Conducting a regular physical inspection cycle to examine hose gaskets, cleanliness, and exterior condition, and replacement of hoses when necessary, to maximize containment integrity.
- Providing adequate facilities and procedures to handle any leaks and spills.
- Directing drainage away from the unloading area. Installation of a collection pit as a containment for spills is recommended.
- Ensuring high-level alarms for storage tanks are audible in the unloading area and control room.
- Using automatic shutoffs can prevent overfilling of storage tanks and reduce the risk of loss of containment.
- Verifying proper operation by periodically testing storage tank high-level alarms and shutoffs.
- Ensuring packing and lubricant for pumps, glands, etc. are of a material compatible with methacrylate ester handling.
- Always avoiding the use of inert gas blanketing which results in less than 5% oxygen content in the vapor space. This is necessary for the effectiveness of the inhibitor to reduce the risk of polymerization.
- Ensuring that the method of unloading has a provision for controlling the flow rate and emergency shut off.
- Avoiding unloading directly into IBCs or drums without a fixed and controllable drum filling system.
- Ensuring access to emergency shower and eyewash facility near the unloading area.
- When samples are required, it is recommended that this is done via an in-line sample valve and not from the bottom valve of the delivering vehicle. Tank top sampling requires safe working at height access and is normally performed by a trained operator and not the delivering driver.

The following PPE is highly recommended or may be legally required whenever making or breaking connections, including bulk unloading:

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

## 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.

The use of compressed air to unload flammable liquids such as MMA can result in an increased fire risk and is not recommended. Increasing oxygen lowers the flash point thereby increasing the risk of fire, and a 21% or lower oxygen concentration is thus recommended to unload or handle flammable liquids. To minimize risk of polymerization a vapor space containing more than 5% oxygen is required. As with other vapor spaces, do not use nitrogen blanketing during unloading operations.

**The following unloading actions for inclusion in procedures are suggested for methacrylate esters to reduce risk of spills, odors and fires.** Prior to connecting or unloading any shipment it is recommended and may be required to verify the delivery contents against documentation, to verify there is space available in the storage tank, and to prepare all unloading equipment. Examples of recommended steps for preparing for unloading include:

1. Positively verifying contents by sampling, verifying the bill of lading description, placard verification, or other means.
2. Locating and testing the operation of the nearest emergency shower and eye wash.
3. Placing warning signs or cordoning off unloading area to restrict personnel entry.
4. Inspecting and wearing required PPE before sampling or making any pipe connections to the truck.
5. Visually inspecting shipping containers for leaks and other irregularities. US Department of Transportation regulations prohibit vehicles from using public roads after a leak is discovered.
6. Verifying that the receiving vessel can hold the entire shipment.
7. Verifying 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.
8. For tank trailers, spotting the trailer, shutting off the engine, setting the brakes, having the driver leave the unloading area, and setting wheel chocks.
9. For rail cars, spotting the car, setting the hand brake, setting wheel chocks, placing "Tank Car Connected" sign on track, and placing derailleurs or lock out switches beyond accessible ends of the rail car.
10. Earth grounding, with positive indication of effective earthing being achieved for the tank trailer or rail car.
11. To prevent personnel exposure, verifying that all valves are closed before removing any caps, plugs, or flanges.
12. Avoiding using split delivery points with multiple off-take connections from a single compartment delivery tank to minimize spillage.
13. Using clean, dedicated piping, equipment, and hoses.

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

1. Connecting the appropriate line to the vent valve on the shipping container and connecting the vapor return hose.
2. Opening the vent valve on the shipping container to equalize the shipping container pressure with the receiving tank, pressure source, or atmosphere. Opening the vapor valve during unloading prevents implosion of the shipping container.
3. Connecting the liquid unloading hose to the shipping container's unloading fitting.
4. Opening 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.
5. Starting the pump.
6. Monitoring hose connections and piping for leaks stopping transfer if leaks occur and checking that the level in the receiving tank rises appropriately. If using vapor return, monitoring the pressure gauge can assure vapor return line is clear and flowing and prevent implosion of the shipping container.
7. Remaining in the unloading area until transfer is complete.
8. When the container is empty, shutting off pump.
9. Closing the unloading valves, including the internal hydraulic valve and external manual valve on tank trucks.
10. Closing the vent valve on the shipping container.
11. Venting and draining the unloading hose, then disconnecting it carefully.
12. Carefully venting and disconnecting vapor return hose.
13. Replacing caps, plugs, and flanges removed for unloading and securing equipment covers.
14. Following appropriate regulations for securing an empty tank truck or rail car for shipment.
15. Disconnecting the ground clamp, removing wheel chocks, "Connected" sign(s), and/or derails, and unlocking railroad switches.

## 9.5 UNLOADING TANK TRUCKS WITH PRESSURE

It is not recommended to unload flammable liquids from tank trucks using pressure. Pressurized air and inert gases pose flammability issues and a polymerization risk for methacrylate esters. In addition, pressurization would increase the potential for significant leakage and increase emissions into the environment. Contact your supplier before considering using pressure unloading.

## 9.6 REFERENCE SOURCE MATERIAL ON TRANSPORTATION

The European Chemical Industry Council (Cefic) Best Practice Guidelines - Cefic develops and promotes guidelines on best practices in transport and logistics operations in close collaboration with the European transport industry.

<http://www.cefic.org/Industry-support/Transport--logistics/Best-Practice-Guidelines1/General-Guidelines-/>

## 10 STORAGE AND HANDLING

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Handling methacrylate monomers safely and ensuring the stability of methacrylate monomers can be achieved by having management procedures and training which build on the following factors:

- Managing the toxicity risks (see Section 6.1)
- Managing the flammability risks (see Section 7)
- Ensuring oxygen is present in vapor spaces (see Section 7.3.4)
- Variation in the effectiveness of inhibitors and the storage life of monomers with temperature (see Section 8.1.1)
- Effect of materials of construction and other equipment design factors on the stability and other properties of monomers. (see Section 8.1)

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; some polymerization inhibitors are more soluble in water, and therefore tend to diffuse out of the monomer phase and into the aqueous phase, reducing monomer stabilization.

It is recommended to read this entire Manual before storing methacrylate monomers or before designing a storage system for methacrylate monomers. Awareness of and implementation of all preventive measures described in this Manual will help minimize the possibility of polymerization occurring.

See Section 8: RESPONSE TO UNCONTROLLED POLYMERIZATION for a full description of polymerization hazards.

## 10.1 DRUM AND IBC STORAGE

Methacrylate monomers are sold in steel or high density polyethylene (HDPE) drums. In some regions reusable stainless steel drums may be used. Intermediate bulk containers (IBCs) of various constructions (including ultraviolet radiation protection) may also be used and treated similarly to drums. Drums and IBC's are generally specified to be electrostatically safe due to the flammability of the materials being stored.

To ensure inhibitor effectiveness, all drums and IBC's are filled to allow for a vapor space containing enough oxygen to meet the shelf life requirements. Oxygen is consumed slowly as part of the free radical scavenging mechanism to prevent polymerization. Consult your supplier for their recommended drum and IBC shelf life.

### Key points:

- The drums and IBC's must be stored according to applicable national, state and local regulations. As a general guide, it is not recommended to store drums and IBC's more than two high. Keeping a path of 1.5 meters (5 feet) free around each block provides for ventilation and both normal and emergency response access.
- Exposure to elevated temperatures can cause polymerization.
- Indoor storage and avoidance of any exposure to the heat of direct sunlight helps reduce polymerization risk.
- Keeping all storage areas well ventilated helps reduce risks.
- Outdoor storage of drums and IBC's without any means of weather protection is not recommended.
- If buildings or other structures are used for the outdoor storage of drums and IBC's, it is recommended that they are constructed using a non-combustible material, are well ventilated, and shield the drums and IBC's from the sun. Underwriters and insurance companies may also impose applicable requirements.
- The amount of oxygen available to support stabilization is limited and exceeding the recommended shelf life is not recommended.

#### 10.1.1 Drum and IBC Handling

When a carload or truckload of drums and IBC's is received, opening the doors carefully reduces the risk of injury. Leaving the doors open for a period allows any potential odors to dissipate before entering. If a strong, persistent odor is present, indicating a leaking container, it is recommended to immediately call the supplier. See Section 11.2: SPILL AND LEAK CONTROL.

### 10.1.2 Drum and IBC Emptying

Before opening drums and IBC's it is recommended to ensure they, as well as all piping and pumping equipment, are well-supported and earth grounded. A static-free dip pipe or flexible stainless-steel hose are normally used to drain the monomers. Ensuring adequate local exhaust ventilation is provided helps minimize personnel exposure and the dangers from spillage and the escape of vapors.

Striking drums and IBC's fittings with tools or other hard objects may cause sparking or puncture, causing a potential danger. The use of non-sparking hand tools when opening flammable monomer drums and IBC's helps to prevent fires, as do good earthing or grounding connections made before starting any work.

**An overhead vapor space must be maintained in the drums and IBC's to provide additional oxygen for polymerization inhibition and to prevent over-pressurizing.** Do not use an inert gas, such as nitrogen, as a vapor pad on any containers.

Wearing the PPE recommended in Section 5.4: PERSONAL PROTECTIVE EQUIPMENT GUIDELINES and the use of a bung or plug wrench can reduce the risk of injury when removing plugs (bungs) from a drum of methacrylate monomers (or opening an IBC). **Note that the drums and IBC's contents may be under pressure or vacuum.**

As the plug starts to loosen, no more than one full turn is generally necessary. If internal pressure exists, slowly allowing it to escape to the atmosphere helps prevent dangerous release of product. After doing so, the operator can loosen the plug further and remove it.

Pumping is the best method to empty drums and IBC's, ensuring that electric pumps comply with the area electrical classification requirements. Drums and IBC's may be emptied by gravity using self-closing valves. Using pressure to displace any container contents poses an increased risk of fire and is not recommended.

Residual vapors in containers may cause an explosion on ignition. Cutting, drilling, grinding, or welding near drums and IBC's could ignite residual material in the container.

### 10.1.3 Drum and IBC Disposal

Empty drums and IBC's are hazardous because of residual liquid and vapor. Dispose of drums and IBC's in accordance with applicable regional, national, state, and local requirements. Improper disposal or reuse of drums and IBCs may be dangerous and illegal.

Washing with water or other suitable materials to remove traces of the methacrylate ester may effectively decontaminate the container before disposing of drums and IBC's. Dispose of rinse water properly in accordance with regulations. See Section 11.2: WASTE DISPOSAL.

## 10.2 BULK STORAGE

Bulk storage facilities are subject to appropriate engineering, safety, and environmental requirements for flammable materials and to regulatory standards and guidelines. It is recommended that best practice guidance be included in hazard and operational reviews.

Diked or bunded areas for storage tanks and pumps reduce the risk of environmental contamination in the event of unintended escape of material and may be required by regulation.

Inclusion of fail-safe positioning of automated valves and emergency backup power for critical instrumentation in the design can reduce risks.

### Key points:

- Methacrylate ester monomers are highly flammable. Suitable design of all bulk storage and transfer systems can minimize ignition risk, as can proper electrical grounding and effective bonding of all connected equipment.
- Store methacrylate monomers under a vapor space atmosphere containing oxygen between 5% and 21% to ensure the polymerization inhibitor used to stabilize the monomer during storage will function.
- Maintenance of a vapor space over the liquid of at least 10% of tank volume helps ensure oxygen is available for polymerization inhibition during storage.
- Never bubble nitrogen through the monomer in storage, or blow lines with nitrogen, lest insufficient oxygen remains available for polymerization inhibition.
- Methacrylate monomers are normally stored at ambient temperatures. Effective monitoring of temperature measurement with appropriate alarm settings serves to warn of possible unscheduled polymerization events. Tanks normally used for methacrylate ester storage in hotter climates may be painted white to minimize heat absorption during the summer months.
- The use of HAZOP or similar risk assessment methodology can allow for the consideration of all potential risks and consequences when planning an installation. Larger bulk quantities of the methacrylate monomers imply potentially higher risk, because of higher potential consequences. It is highly recommended to have in place, and review regularly, mitigation plans that address all significant risks.
- Positioning tanks and pumps in a diked or bunded area reduces risk of environmental contamination in the event of unintended escape of material.
- The most common design for an above ground tank incorporates a vertical shell, a flat bottom and a conical top. Proper design allows for uniform mixing of the contents with new deliveries. A tank pad and dike that give enough bund capacity in the event of a major loss of containment will help prevent spread of the released material. Not all concrete specifications are compatible with methacrylate esters. A tank well with a bottom drain line through the tank pad provides complete tank drainage.
- Underground storage tanks (UST) present an increased risk of loss of containment into the ground. There are therefore specific regulations for UST's in addition to the guidelines for above ground tanks. These will differ by location.



- Suppliers can provide information on special design features required to cope with specific hazards of bulk storage.
- A hazard review and/or risk analysis of the storage facility can help ensure adequate safeguards are in place to reduce the risk of polymerization and exposure.
- An effective maintenance plan including instrumentation and control devices can play a key role in reducing risks.
- Training of personnel in the operation of the storage systems and control devices for both normal use and emergency response minimizes any risks associated with storing methacrylate esters.
- Stainless and carbon steels are suitable materials of construction. If carbon steel is to be used, formation of internal rust may cause product contamination; preparing internal surfaces before bringing into service may help to reduce the risk of such contamination.

The optimum capacity for a storage tank is a function of the volume, the frequency of deliveries of monomer and the rate of use. For the efficient scheduling of deliveries, it is recommended that storage tanks have a minimum capacity of 1.5 times the volume of the typical expected delivery volume.

#### 10.2.1 Elimination of ignition sources

Methacrylate esters flowing through or being discharged from a pipeline may generate static electricity. Electrically interconnecting (bonding) and proper earthing/grounding of all equipment reduces static and the resulting risk of ignition.

The use of a dip tube avoids splash filling into a tank and associated hazards of static generation. If mixing nozzles are used in storage tanks, keeping the nozzles well below the liquid surface avoids spraying, which may cause static charge generation.

See Section 6.2 for more information.

#### 10.2.2 Pressure Relief

##### **Key points:**

- A runaway methacrylate ester polymerization reaction will generate temperatures greater than the monomer boiling point. There is no guaranteed or warranted method for relieving the pressure from such a runaway with the consequent potential for rupture of the tank or container. Therefore, low design pressure (API atmospheric) tanks are recommended.
- While there is no experience with runaway reactions in full-size tanks available, weak seam or frangible roof designs are believed to provide the best protection from a failure. The use of roof guide cables to provide attachment restraint for this type of roof may be considered. Alternatively, oversized rupture disks or weight-loaded lids (“weighted manway cover”) may be considered.

- Emergency venting devices normally used for flammable liquids are considered to give adequate fire protection. However, this type of device may not provide adequate relief in the event of an uncontrolled or runaway polymerization where two-phase expansion may be possible.
- To allow natural tank breathing, a conservation valve is normally installed. Various designs such as weighted pallet or breathing valves with flexible diaphragms are commercially available.
- Methacrylate ester vapors evaporating from the bulk liquid surface do not contain any stabilizers. These unsterilized monomer vapors can condense on surfaces such as relief valve inlets, rupture disks or dead legs in piping, and may then polymerize. Ensuring that pressure relief devices and their connected lines are free-draining and without pockets where liquid may accumulate helps to prevent this hazard. It is recommended that vent lines are checked periodically for the presence of polymer which may result in interference with their proper operation. Relief valves and nozzles may be electrically traced and insulated to help control polymer formation by preventing condensation. To prevent condensation, the temperature setting of the tracing needs to be higher than the condensing temperature expected in the nozzle.
- A vent line and associated devices help 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. Establishment and implementation of an inspection schedule can help ensure there have been no polymer blockages formed by condensed uninhibited monomer.
- The use of VOC reduction equipment such as containment of vapors with closed loop unloading or venting through a scrubber or incinerator may be considered.

### 10.2.3 Temperature Measurement

Two separate temperature measurement instruments in each storage tank, ideally spaced at 180 degrees around the circumference of the tank, are normally used to measure the liquid temperature near to the tank bottom. In larger tanks, it may be advantageous to have a third measurement point installed at approximately one third of maximum liquid height when measured from the bottom.

Temperature monitoring systems are typically capable of determining the absolute temperature of the bulk liquid as well as the rate of temperature rise. Continuous level readout, including at remote locations, with alarm capabilities helps to ensure potential polymerization is detected early. Recording the temperature is helpful in allowing trends to be monitored easily. Temperature alarms will warn of potential polymerization risk with high alarms set to activate at a temperature about 5°C above the normal maximum temperature of the stored liquid. Temperature indication and recording allows any rate of change in storage to be monitored.

An effective testing and maintenance plan for all instrumentation is highly recommended to ensure safe operation.

#### 10.2.4 Level Instruments

Continuous level readout, including at remote locations, with alarm capabilities is recommended to prevent overflowing and loss of containment. A high-level alarm at 85-90% of the tank capacity is suggested, coupled with a high-level switch set at 90-95% which closes the valve on the tank inlet feed line.

There are many different types of level measurement available. The key criteria after accuracy and reliability are compatibility with flammable and polymerizing substances. Level measurement devices are ideally non-contact and without any narrow tubes or crevices with limited flow.

#### 10.2.5 Pumps

Positioning pumps away from any heat source such as radiators or steam pipes avoids overheating. Overheating of pumps on methacrylic ester duty can cause polymerization, which may result in containment failure or other consequences. Some options to help protect pumps from overheating are:

- A temperature sensor placed inside the pump or close to the discharge which activates an alarm and shutdown switches if a high temperature is detected. Deadheading a centrifugal pump can cause a rapid rise in temperature inside the pump
- A power monitor that senses low power consumption and activates an alarm and shutdown switch. Deadheading a centrifugal pump usually results in an immediate reduction in power consumption.
- A flow detection element on the discharge line that activates an alarm and shutdown switch when a low flow is detected. A properly located low flow element connected to a shutdown switch can provide deadhead protection.
- A liquid sensor element placed in the suction line or feed vessel that activates an alarm and shutdown switch when liquid is not detected. This sensor can be used to help avoid running a pump dry but does not give deadhead protection. Many types of pumps quickly overheat if operated dry.
- Two different types of sensing elements may be installed in order to provide redundant protection from pump overheating.
- Regular assessment of trips, interlocks and system integrity is recommended to ensure reliability and effective protection.

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. Seals and bearings in contact with methacrylic ester may be flushed for adequate cooling and lubrication. High surface temperatures can cause polymer particles to form. Centrifugal pumps either packed or with a gliding disk seal, may require more maintenance due to the poor lubrication properties of the methacrylate monomers.

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, installation of a low flow switch or level control device can protect pumps from dry operation or deadheading, as the heat generated during operation without flow can initiate polymerization. Having a low power alarm function for canned pumps is an indicator of low flow and so may be used to indicate any loss of flow and hence risk of overheating. High power usage is an indication of potential malfunction.

Air-driven diaphragm pumps are occasionally used for acrylate service. Diaphragm pumps usually stop pumping if deadheaded and may not require instrument interlocks to protect against overheating.

Use of truck-mounted pumps for unloading methacrylic ester presents the potential for contamination, leaks and overheating and is thus not recommended.

#### 10.2.6 Piping and Transfer Lines

Ensuring that transfer lines are never positioned close to a heat source such as radiators or steam pipes helps prevent unintended polymerization.

After construction, cleaning all piping of grease and scale residues that may be adhering to the inner walls helps prevent contamination. Where high local ambient temperatures and solar gain may be expected, measures to minimize these effects will reduce the risk of polymerization.

Sloped piping to allow for free draining and avoiding dead-legs helps prevent pooling of the monomer. Trace heating may be considered if condensation of monomer vapors is expected.

It is recommended to drain and clear pipelines and associated systems that are liquid filled when they will be dormant or taken out of regular service for any length of time, as any residual monomer remaining in the lines may polymerize.

#### **CAUTION:**

**Do not use inert gas (nitrogen or other non-oxygen containing gas) to blow pipelines clean. Blowing pipelines clean with a mixed gas with at least 5% oxygen, as opposed to an inert gas like nitrogen, is necessary to preserve polymerization inhibition.**

**Blowing flammable material lines with air can cause an ignition risk if a static charge develops. Effective earth bonding helps limit this risk. In some locations, 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. Systems can be designed to avoid these potential problems.**

To limit vapor emissions during monomer transfers, it is recommended 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. A slight inclination toward the storage tank in the vapor return line (back-venting pipe) in a closed loop unloading system will allow condensed liquid to drain back into the tank. A shut-off valve in the vapor return line on the end connected to the transport vessel helps prevent vapor escape. Some local regulations may also require a flame arrestor on the end close to the tank.

### 10.2.7 Materials of Construction

Proper choice of materials of construction is important for safety, health, and protection of the environment.

The preferred construction material for tanks, pumps and pipes is stainless steel (e.g. EN 58 C or H; DIN 1.4571 or 1.4541; US 304L, 316L or 321) or carbon steel.

If carbon steel is to be used, it is strongly recommended to prepare the tank for use before introducing methacrylate esters. To prevent rust, sand blast and then clean the tank before use. After sand blasting and prior to introduction of monomers it is also recommended that the tank is nitrogen blanketed.

Polyethylene, polypropylene, or fluoropolymers are also suitable as materials of construction for methacrylate monomer equipment and may be useful for accessory equipment such as gaskets and valve parts. Preferred gaskets are made of PTFE (polytetrafluoroethylene), cross-linked EPDM (ethylene propylene diene monomer), or stainless steel with graphite coating or Kalrez®.

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 that cotton has been known to shed small fibers, which can cause contamination. Careful selection of materials helps reduce the risk of loss of containment and contamination.

### 10.2.8 Vapor scrubbing

A wet scrubber using an aqueous caustic solution with organic amines can efficiently treat methacrylate ester vapors.

#### **CAUTION: Carbon absorption filters**

For the final off-gas purification and odor elimination, an active carbon cartridge may be used if protected from receiving high organic loadings. The heat of adsorption on active carbon is unusually high for all methacrylate monomers so it is possible for ignition to occur if highly vapor loaded exhaust gases contact active carbon. Incidents with carbon adsorbers on methacrylate ester duty have been reported.

**CAUTION: To prevent hazardous ignition incidents, before considering active carbon cartridges for the removal of methacrylate esters from storage vent gases, undertake a rigorous hazard and operability study and mitigate all known risks associated with this type of unit.**

If carbon filters are considered, it is recommended to locate them away from process areas and fit them with either inlet and outlet temperature measurement, or preferably Carbon Monoxide monitoring and alarm instrumentation. Maintaining a low VOC loading on the adsorber, for example by using a scrubber upstream of the carbon bed, minimizes risks. Fitting a flame suppression system between any carbon adsorber and the bulk liquid may also help to reduce risks.

## 10.3 REFERENCE SOURCE MATERIAL ON TRANSPORTATION

### 10.3.1 UK Health and Safety Executive (HSE)

The HSE publishes three guidance documents dealing with fire and explosion hazards associated with flammable liquids. The following are available to download free of charge:

- **HSG 176 - The storage of flammable liquids in tanks** - According to the HSE, “This guidance applies to above and below ground fixed bulk storage tanks. It applies to premises where flammable liquids are stored in individual tanks or groups of tanks. It may also be applied to portable or skid-mounted vessels with capacities more than 1000 liters.

It also gives guidance on the design, construction, operation and maintenance of installation used for the storage of flammable liquids in fixed and transportable tanks operating at or near atmospheric pressure.

It will help you assess the risks arising from the use of flammable liquids and decide how to control those risks.”

<http://www.hse.gov.uk/pubns/books/hsg176.htm>

- **HSG 51 - The storage of flammable liquids in containers** - According to the HSE: “This guidance is for those responsible for the safe storage of flammable liquids in containers at the workplace. It applies to storage of flammable liquids in containers up to 1000 liters capacity.

It explains the fire and explosion hazards associated with flammable liquids and will help you determine how to control the risks in your workplace.”

<http://www.hse.gov.uk/pubns/books/hsg51.htm>

- **HSG 140 - Safe use and handling of flammable liquids** - According to the HSE: “This guidance is for those responsible for the safe use and handling of flammable liquids in all general work activities, small-scale chemical processing and spraying processes.

It explains the fire and explosion hazards associated with flammable liquids and will help you determine how to control the risks in your workplace.”

<http://www.hse.gov.uk/pubns/books/hsg140.htm>

### 10.3.2 US Occupational Safety and Health Administration

The US regulations governing the storage of flammable chemicals are covered in:

Code of Federal Regulations (CFR)

Title 29

Labor

Part 1910

Occupational Safety and Health Standards

Subpart H

Hazardous Materials

Standard 1910.106

Flammable liquids

<https://www.osha.gov/law-regs.html>

## 11 ENVIRONMENTAL CONSIDERATIONS

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**Governmental regulations governing waste disposal generally require that producers and users of chemical products be fully aware of viable alternatives for the safe disposal of waste materials and select and practice a disposal method or process that assures compliance with all applicable requirements. The required treatment or disposal of methacrylate esters 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 in general all controlled by governmental (local, regional, national, and international) laws and regulations. Noncompliance can be subject to criminal or civil penalties, or both. Spills must be promptly reported to appropriate authorities and cleaned up in accordance with applicable regulations.

### 11.1 ENVIRONMENTAL IMPACT SUMMARY

*The persistence of methyl methacrylate in the atmosphere is short, and the chemical is not considered to contribute directly to depletion of the ozone layer. Methyl methacrylate is not expected to bioconcentrate in the environment, and inhalation from air is likely the primary route of human exposure.*

*WHO (CICAD 4: 1998)*

Methacrylate ester monomers are not classified as harmful to the environment because of generally low aquatic toxicity, rapid biodegradation, and low persistence and bioaccumulation. Available data indicates that low molecular weight methacrylate monomers are of low toxicity to aquatic organisms. Methacrylate ester monomers are also fully and rapidly biodegradable, and while they are not normally intentionally released during manufacturing processes and use, monomer released to the air or trace amounts present in wastewater streams would be rapidly broken down because of chemical and biological degradation. Methacrylate ester monomers do not possess a significant ozone depletion potential and trace emissions do not contribute significantly to global warming.

Additional information may be obtained from the SDS supplied by the manufacturer.

The following table includes information for testing performed with the concentrated substances.

	MMA	EMA	n-BMA	i-BMA	2-EHMA
Ecotoxicity	Low toxicity to aquatic organisms.				Harmful to aquatic life with long lasting effects
Persistence and degradability	Readily biodegradable substantially removed in biological treatment processes				
Bio-accumulative potential	Low potential for bioaccumulation		Moderate potential for bioaccumulation	Moderate potential for bioaccumulation though like other methacrylate esters they are readily degraded and therefore have a low potential	High potential for bioaccumulation but data from a fish bioconcentration test indicate a low potential
Mobility in soil	Predicted to have high mobility in soil.		Predicted to have moderate mobility in soil		
Results of PBT and vPvB assessment	Not classified as PBT or vPvB				

PBT: Persistent; Bioaccumulative; Toxic

vPvB: very Persistent; very Bioaccumulative

Source - Registration dossier - <https://echa.europa.eu/search-for-chemicals>

### 11.1.1 Methacrylate Ester Environmental Fate and Degradation

The basic methacrylate esters are not persistent in the environment. The two main degradation pathways are biodegradation and photo degradation.

In water the lower molecular weight methacrylate esters biodegrade quickly. All substances are rapidly biodegraded by bacteria present in water and sewage treatment plants. Laboratory test data show ready biodegradation with complete mineralization. While methacrylate ester monomers are not intentionally released during manufacturing processes and use, trace amounts present in wastewater streams would rapidly be broken down by biological degradation and evaporation. Due to rapid degradation, they do not enter the food chain.

In air, the methacrylate monomers react with photo-chemically produced hydroxyl radicals and also with ozone. Half-lives for these reactions have been estimated with the EPI Suite™ program as provided by the United States Environmental Protection Agency (US EPA). The reaction half-lives for the atmospheric oxidation of the methacrylate esters by hydroxyl radicals range between 6.9 h (MAA), 7.0 h (MMA), 6.5 h (EMA), 5.7 h (n-/i-BMA) and 4.4 h (2-EHMA) with a slight trend of shorter half-lives with increasing molecular weight. For the reaction with ozone, an atmospheric half-life of approximately one day has been calculated for all esters.

The substances do not possess a significant ozone depletion potential and trace emissions do not contribute significantly to global warming.



### 11.1.2 Methacrylate Ester Ecotoxicity

The ecotoxicity of the basic methacrylate esters has been reviewed extensively under WHO (CICAD 4: 1998) and OECD Existing Chemicals Risk Assessment programs (OECD 2001 and 2009). Based on the available data, the reviews concluded that the esters are of low to high toxicity to aquatic organisms. The toxicity increases with increasing lipophilicity and molecular size across the category with MAA, MMA and EMA being the least toxic and 2-EHMA the most toxic. This trend was consistent between all three trophic levels studied (algae, daphnia and fish) as was the general level of toxicity.

In summary, the OECD assessment concludes that “the category members possess properties indicating a hazard for the environment (acute toxicity between 1 and 100 mg/L). However, the chemicals in this category are of low priority for further work because of their rapid biodegradation and their limited potential for bioaccumulation.”

A comparison of the ecotoxicity data of the methacrylate esters and emission data indicate that under operating parameters of the methacrylate industry they do not pose a risk to the environment.

### 11.1.3 References

- **European chemicals Agency (ECHA)** – <https://echa.europa.eu/>  
The ECHA Registered Substances database contains a summary of current environmental fate and ecotoxicological information on methacrylate esters. This database, per the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation, is continuously updated with new information, and can be searched here: <https://echa.europa.eu/information-on-chemicals/registered-substances>.  
REACH Registration Dossiers contain specific information on environmental fate and ecotoxicity, and can be found here:
  - MMA (80-62-6): <https://echa.europa.eu/registration-dossier/-/registered-dossier/15528>
  - EMA (97-63-2): <https://echa.europa.eu/registration-dossier/-/registered-dossier/13871>
  - n-BMA (97-88-1): <https://echa.europa.eu/registration-dossier/-/registered-dossier/15151>
  - i-BMA (97-86-9): <https://echa.europa.eu/registration-dossier/-/registered-dossier/14969>
  - 2-EHMA (688-84-6): <https://echa.europa.eu/registration-dossier/-/registered-dossier/14761>
- **WHO Concise International Chemical Assessment Document 4: Methyl Methacrylate** - <http://www.who.int/ipcs/publications/cicad/en/cicad04.pdf>  
“The **International Programme on Chemical Safety (IPCS)**, established in 1980, is a joint venture of the United Nations Environment Programme (UNEP), the International Labour Organisation (ILO), and the World Health Organization (WHO). The overall objectives of the IPCS are to establish the scientific basis for assessment of the risk to human health and the environment from exposure to chemicals, through international peer review processes, as a prerequisite for the promotion of chemical safety, and to provide technical assistance in strengthening national capacities for the sound management of chemicals.”

- **OECD Existing Chemicals Database** - <http://webnet.oecd.org/hpv/ui/Search.aspx>  
OECD Screening Information Data Sets (SIDS) are the summary reports bringing together all the information needed for health and environmental risk assessment of chemicals. These reports include the following information:
  - General Substance Information
  - Information on Exposure and Use
  - Physical Chemical Data
  - Environmental Fate and Pathways
  - Ecotoxicity Data
  - Human Health Data, including Experience with Human Exposure if available

The reports available for the Methacrylate Esters included in this guide are:

- OECD, 2001 - OECD SIDS/SIAP/SIAR Methacrylic acid, CAS no. 79-41-4
- OECD, 2001 - OECD SIDS/SIAP/SIAR Methyl Methacrylate, CAS no. 80-62-6
- OECD, 2009 - SIDS/SIAP/SIAR Category Short-chain Alkyl Methacrylates (assessment referring to ethyl methacrylate, n- and iso-butyl methacrylate and 2-ethylhexyl methacrylate)
- See also: Staples CA, Farr C, Hunt EK, McLaughlin JE, Müllerschön H, Pemberton MA, 2009. Using Quantitative Structure–Activity Relationships to Support the Assessment of the Environmental Fate and Aquatic Toxicity of a Series of Methacrylic Acid Esters, Human and Ecological Risk Assessment, 15: 503–525

## 11.2 WASTE DISPOSAL

Local regional, national, and international regulations govern waste disposal, and full awareness by producers, suppliers, carriers, and users of monomers of viable options for the disposal of materials containing methacrylate esters will help ensure compliance with these regulations. Materials to be disposed of include residues from production and cleaning operations as well as waste material from spills.

Methacrylate ester wastes generally have a particular classification and required treatment under national regulations. For example, MMA and EMA 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 and U118 for EMA. n-BMA and i-BMA are “characteristic wastes” under RCRA, based on ignitability (designated D001). 2-EHMA is not a RCRA hazardous waste. In the EU, wastes are classified according to EU Directive 2008/98/EC on Waste (as amended by EU Directive 2018/851). Hazardous wastes are either marked on the “list of waste” (Commission Decision 2000/532/EC) or classified by member states. Member states have the ability to consider a waste hazardous if the waste contains a substance which is classified as hazardous under the classification, labeling and packaging (CLP) regulation (EC 1272/2008) (see Annex III of EU Directive 2018/851). Most methacrylate esters are classified as flammable liquids under the CLP regulation, and therefore are also considered “hazardous wastes.” In the UK, methacrylate esters are classified as “hazardous” under the UK Hazardous Waste Regulations (2005). In the UK, hazardous wastes may include, but are 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, generally with the local authority's knowledge and approval. Disposal of absorbents or polymeric material containing methacrylate esters is normally done 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, keeping methacrylate esters separate from incompatible materials, such as peroxides, helps to prevent polymerization.

### **11.3 SPILL AND LEAK CONTROL**

Careful design and good operating procedures will minimize the risk from leaks and spills. Written spill and leak response procedures are recommended and may be required by law.

Proper design and on-going operation of facilities helps ensure that even minor leaks or spills cannot enter unsuitable drainage systems or the wider environment. Prompt notification of responsible pollution control agencies may be required if methacrylate esters are released into surface water or to a municipal sewer system. Awareness by facilities handling methacrylate esters of the local rules for release reporting and public information concerning hazardous chemicals in the community helps prevent liability.

Small spills of up to 5 liters can normally be suitably absorbed in commercially available spill cleanup kits. Locating facilities within diked or bunded areas can contain larger spillages. Spills outside of these areas can be contained temporarily by stacking sand bags or similar absorbent material. Avoiding run-off into storm sewers routed to public waters prevents wider contamination.

In the US, MMA and EMA have Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) Reporting Quantities (RQ) of 1000 pounds when released or spilled into the environment (40 C.F.R. sec. 304.2). The National Response Center (NRC) must be notified (1-800-424-8802) in the event of a release or spill greater than 1000 pounds (40 C.F.R. sec. 302.6). Under the Superfund Amendments and Reauthorization Act (SARA) Title III Section 311/312, all chemical requiring an SDS under OSHA regulations are hazardous chemicals, requiring local community notifications; this would include the methacrylate esters. 40 C.F.R. Part 370. MMA is also a SARA Section 313 chemical, for which annual reporting of releases from point sources and fugitive emissions at certain facilities are to be reported (40 C.F.R. Part 372).

In the UK releases of methacrylate esters must be reported as per the Reporting of Injuries, Diseases and Dangerous Occurrences (RIDDOR) Regulations 2013. Other regulatory authorities have differing requirements.

## 11.4 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. For example, like most organic chemicals, methacrylate esters are classified as Volatile Organic Compounds (VOCs) under the US Clean Air Act and therefore may be subject to limitations on VOC emissions. MMA is listed by the US EPA as a Hazardous Air Pollutant (HAP) under Section 112(b) of the Clean Air Act Amendments of 1990. In the EU, the storage and use of methacrylate esters may fall under Directive 2010/75/EU on Industrial Emissions and the REACH Regulation (Regulation (EC) No. 1907/2006). Users are responsible to ensure that their air emissions are in compliance with any applicable laws and regulations.

Direct emissions to the atmosphere above certain levels are generally required to be controlled and permitted by national and/or local authorities. Closed loop or vapor balancing unloading can be effective in reducing and controlling unloading emissions and odors. It is recommended that closed loop unloading is provided for storage facilities. If there is a common vent header for multiple storage tanks on differing duties, however, there is a potential for contamination. Methacrylate ester vapors are uninhibited, and if these vapors condense and collect in the vapor return system they may polymerize, causing blockages. Specifying systems to drain back into the bulk of the product and avoiding the creation of dead legs where condensed vapor can collect helps prevent pooling and polymerization.

It is recommended, and may be required, that exhaust gases rich in methacrylate esters are treated 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 SDS for more complete and up to date information.