Safe Handling and Storage of Acrylic Esters

EBAM
European Basic Acrylic Monomer Group
Safe Handling
and Storage of Acrylic Esters
Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Preface</td>
<td>6</td>
</tr>
<tr>
<td>2. Names and Codes</td>
<td>7</td>
</tr>
<tr>
<td>3. Potential Hazards</td>
<td>7</td>
</tr>
<tr>
<td>4. Potential Hazards</td>
<td>7</td>
</tr>
<tr>
<td>4.1 Polymerisation</td>
<td>7</td>
</tr>
<tr>
<td>4.1.1 Polymerisation caused by overheating</td>
<td>7</td>
</tr>
<tr>
<td>4.1.2 Polymerisation caused by oxygen depletion</td>
<td>9</td>
</tr>
<tr>
<td>4.2 Fire and Explosion Hazards</td>
<td>10</td>
</tr>
<tr>
<td>5. Health and Safety Factors</td>
<td>11</td>
</tr>
<tr>
<td>5.1 Toxicity</td>
<td>11</td>
</tr>
<tr>
<td>5.2 Industrial Hygiene</td>
<td>11</td>
</tr>
<tr>
<td>5.3 First Aid</td>
<td>12</td>
</tr>
<tr>
<td>5.3.1 First Aid in case of eye contact</td>
<td>12</td>
</tr>
<tr>
<td>5.3.2 First Aid in case of skin contact</td>
<td>12</td>
</tr>
<tr>
<td>5.3.3 First Aid in case of inhalation</td>
<td>13</td>
</tr>
<tr>
<td>5.3.4 First Aid in case of ingestion</td>
<td>13</td>
</tr>
<tr>
<td>6. General Considerations for Transport and Storage</td>
<td>14</td>
</tr>
<tr>
<td>6.1 Temperature</td>
<td>14</td>
</tr>
<tr>
<td>6.2 Duration of Storage</td>
<td>14</td>
</tr>
<tr>
<td>6.3 Labelling</td>
<td>15</td>
</tr>
<tr>
<td>7. Bulk Storage Facilities and Accessories</td>
<td>16</td>
</tr>
<tr>
<td>7.1 General Considerations</td>
<td>16</td>
</tr>
<tr>
<td>7.2 Design Considerations</td>
<td>17</td>
</tr>
<tr>
<td>7.2.1 Temperature Control of Bulk Storage Tanks and Accessories</td>
<td>17</td>
</tr>
<tr>
<td>7.2.2. Pumps and Protection of Pumps from Overheating</td>
<td>17</td>
</tr>
<tr>
<td>7.2.3. Detecting Unsafe Conditions Inside Bulk Storage Vessels</td>
<td>18</td>
</tr>
<tr>
<td>7.2.4. Avoiding Polymer Formation in Vent Nozzles and Lines</td>
<td>18</td>
</tr>
<tr>
<td>7.2.5. Indoor Acrylic Ester Storage Facilities</td>
<td>18</td>
</tr>
<tr>
<td>7.2.6. Engineering Features for Environmental Protection</td>
<td>19</td>
</tr>
<tr>
<td>7.2.7. Engineering Considerations for Fire Control</td>
<td>19</td>
</tr>
<tr>
<td>7.2.8. Materials for Construction and Sealing in Acrylic Ester Service</td>
<td>19</td>
</tr>
<tr>
<td>7.2.9. Venting of Bulk Storage Tanks</td>
<td>19</td>
</tr>
<tr>
<td>7.2.10. Emergency Venting of Bulk Storage Tanks</td>
<td>20</td>
</tr>
<tr>
<td>7.2.11. Other Bulk Storage Tank Accessories</td>
<td>20</td>
</tr>
<tr>
<td>8. Equipment Preparation and Cleaning</td>
<td>21</td>
</tr>
<tr>
<td>8.1. General considerations</td>
<td>21</td>
</tr>
<tr>
<td>8.2. Commissioning and decommissioning of tanks</td>
<td>21</td>
</tr>
<tr>
<td>9. Safe Transport of Acrylic Esters</td>
<td>21</td>
</tr>
<tr>
<td>9.1. Personal protective equipment for loading, unloading and handling</td>
<td>21</td>
</tr>
<tr>
<td>9.2. General considerations</td>
<td>21</td>
</tr>
</tbody>
</table>
Introduction

The European Basic Acrylic Monomer Manufacturers Association (EBAM) is the European organisation which represents the European producers of acrylic monomers within the framework of the European Chemical Industry Council (CEFIC). Member companies are BASF SE, ARKEMA, Evonik Stockhausen GmbH, DOW Europe GmbH, Sasol Chemie & Co. KG, ROHM & HAAS Europe Sarl and HEXION Specialty Chemicals, a.s.

The purpose of this brochure is to provide all persons who will use, handle, or otherwise be exposed to acrylic esters with information about their safe handling and storage.

Acrylic esters are flammable or combustible liquids with unusually low odour threshold values. Liquid acrylic esters and their vapours are irritating to the skin, eyes, nose and throat and in most cases are sensitising. Goggles, face shields, protective clothing and rubber gloves should be worn when handling acrylic esters. Begin first aid immediately in all cases of exposure to acrylic monomers (First aid - See Section 5.3).

The full text of this publication should be consulted for information on the hazards of acrylic esters and suggestions for its safe handling and storage. In addition, Material Safety Data Sheets (MSDS) should be requested from the manufacturer. The MSDS may provide more specific detailed information.

The information provided in this pamphlet is believed to be factual. The information is made available “as is” and no warranties are given or liabilities of any kind are assumed with respect to such information, including, but not limited to, its fitness for the purpose, non-infringement of third party rights, or its correctness. EBAM does not assume any legal responsibility for the given data or suggested technical design features. The information does not alleviate the customer from examining the applicability to customer’s specific situation and requirements. It is the customer’s responsibility to ensure that proprietary rights and existing laws are observed.

EBAM can be contacted at the following address:

European Basic Acrylic Manufacturer Association
Attn. Mr. Paul Teheux
Avenue E. van Nieuwenhuyse 4, Box 2
B-1160 Brussels
Tel: (Int. + 32)-2 676 72 58
Fax: (Int. + 32)-2 676 72 16
E-mail: pte@cefic.be

Acknowledgement: EBAM is grateful for the valuable contributions and peer reviewing of this document by the US industry organisation Intercompany Committee for the Safe Handling of Acrylic Monomers ICSHAM. The member companies of ICSHAM are

BASF Corporation
ARKEMA Chemicals Inc
The Dow Chemical Company
Rohm & Haas Company
1. Preface

The purpose of this document is to provide general information on safe handling and storing of basic acrylic esters and how to appropriately deal with the specific hazards comprising health and environmental risks, flammability, and the potential for untimely polymerisations. Prior to working with acrylic esters the Material Safety Data Sheets (MSDS) should be consulted.

Properties and characteristics contained in this document refer to basic acrylic esters with a minimum content of 99 weight %. They conform to the specifications reported in the technical information bulletins issued by the manufacturers. Some of the physical data may be subject to minor changes due to variable concentrations of natural impurities. Basic acrylic esters are commonly stabilised with 15 parts per million (ppm) of monomethyl ether of hydroquinone (MeHQ).

2. Names and Codes

The designation basic acrylic esters refers to the esters of the acrylic acid with methanol, ethanol, n-butanol and the 2-ethylhexanol. In table 1 generic names, synonyms, and international identification codes are listed.

3. Properties and Characteristics

A distinctive property of all basic acrylic esters is their unusually low odour threshold (see Table 1). Working with acrylic esters therefore requires good housekeeping practices in order to prevent odour nuisances from residential and industrial neighbours. An overview of important characteristics and physical properties is given in table 3.

<table>
<thead>
<tr>
<th>Odour Threshold</th>
<th>Recognition %</th>
<th>50</th>
<th>100</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions *)</td>
<td>ppb</td>
<td>ppb</td>
<td>µg/m³</td>
<td>µg/m³</td>
<td></td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>3</td>
<td>20</td>
<td>10</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Ethyl acrylate</td>
<td>0,5</td>
<td>2</td>
<td>2</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>n-Butyl acrylate</td>
<td>0,2</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2-Ethylhexyl acrylate</td>
<td>70</td>
<td>180</td>
<td>525</td>
<td>1350</td>
<td></td>
</tr>
</tbody>
</table>

*) Calculated as: [ µg/m³ ] = [ ppm ] x MW / 24,45

4. Potential Hazards

4.1 Polymerisation

One of the prevailing characteristics of acrylic esters is their high reactivity in the presence of free radicals. Free radicals can be generated by heat, light or irradiation of X-rays and by activation of radical forming materials. Many substances are known to readily promote polymerisation, such as peroxides, peroxide forming and other free radical forming compounds (aldehydes, amines, azides, ethers, nitric acid). Redox-reactions of polyvalent heavy metal ions or hydrolysis of metals with strong mineral acids may likewise initiate a polymerisation. Moisture enhances the likelihood of a polymerisation. Material recycled from production should never be returned to storage tanks designated for fresh monomers.

If procedures for proper and safe handling are not regarded, runaway polymerisations may occur. Depending on external conditions, the polymerisation can proceed with moderate speed, or under unfavourable conditions, with an explosive-like violence. An explosion hazard exists also, if large clouds of vapour escape from the storage container (e.g. due to the heat of polymerisation). If the container is poorly vented, pressure build up may occur rapidly and can lead to the rupture of the vessel. High temperatures caused by a runaway reaction can provide a serious risk of the reacting mass self-igniting.

Acrylic esters are commonly stabilised with 10 to 20 ppm MeHQ (monomethyl ether of hydroquinone or p-
methoxyphenol) to ensure protection from an untimely polymerisation. This stabilisation inhibitor requires oxygen to perform. This protection is only effective at moderate ambient temperatures and for handling conditions described in the following sections.

### Table 2

<table>
<thead>
<tr>
<th>Generic Name</th>
<th>Methyl acrylate</th>
<th>Ethyl acrylate</th>
<th>n-Butyl acrylate</th>
<th>2-Ethylhexyl acrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS name</td>
<td>Methyl 2-propenoate</td>
<td>Ethyl 2-propenoate</td>
<td>n-Butyl 2-propenoate</td>
<td>Acrylic acid n-butylerster</td>
</tr>
<tr>
<td>Synonyms</td>
<td>Acrylic acid methylester</td>
<td>Acrylic acid ethylester</td>
<td>Acrylic acid n-butylerster</td>
<td>Acrylic acid 2-ethylhexylester</td>
</tr>
<tr>
<td>CAS number</td>
<td>96-33-3</td>
<td>140-88-5</td>
<td>141-32-2</td>
<td>103-11-7</td>
</tr>
<tr>
<td>EINECS number</td>
<td>202-500-6</td>
<td>205-438-8</td>
<td>205-480-7</td>
<td>203-080-7</td>
</tr>
<tr>
<td>United Nations number</td>
<td>UN1919</td>
<td>UN1917</td>
<td>UN2348</td>
<td>no UN No.</td>
</tr>
<tr>
<td>EC number</td>
<td>607-034-00-0</td>
<td>607-032-00-X</td>
<td>607-062-00-3</td>
<td>607-107-00-7</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>CH2=CH-COO-CH3</td>
<td>CH2=CH-COOCH2CH3</td>
<td>CH2=CH-COOCH2CH2CH3</td>
<td>CH2=CH-COO-CH2CH2CH2CH2CH3</td>
</tr>
<tr>
<td>Stoichiometric formula</td>
<td>C4H6O2</td>
<td>C5H8O2</td>
<td>C7H12O2</td>
<td>C11H20O2</td>
</tr>
<tr>
<td>Molar mass</td>
<td>86,09</td>
<td>100,12</td>
<td>128,17</td>
<td>184,28</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Methyl acrylate</th>
<th>Ethyl acrylate</th>
<th>n-Butyl acrylate</th>
<th>2-Ethylhexyl acrylate</th>
<th>Dimension</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical state</td>
<td>clear liquid</td>
<td>clear liquid</td>
<td>clear liquid</td>
<td>clear liquid</td>
<td>° C</td>
<td>BS 523</td>
</tr>
<tr>
<td>Solidification temperature</td>
<td>-77 to -75</td>
<td>-72 to -71</td>
<td>147 to 148</td>
<td>90</td>
<td>DIN 51751</td>
<td></td>
</tr>
<tr>
<td>Vapour pressure at K</td>
<td>273</td>
<td>30,8</td>
<td>12,0</td>
<td>1,4</td>
<td>0,02</td>
<td>hPa</td>
</tr>
<tr>
<td>293</td>
<td>90,5</td>
<td>39,4</td>
<td>5,44</td>
<td>0,16</td>
<td>hPa</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>340</td>
<td>168</td>
<td>28,4</td>
<td>1,33</td>
<td>hPa</td>
<td></td>
</tr>
<tr>
<td>Flash point (closed cup)</td>
<td>3 to -2</td>
<td>8 to 9</td>
<td>36 to 40</td>
<td>82 to 87</td>
<td>° C</td>
<td></td>
</tr>
<tr>
<td>(open cup)</td>
<td>2 to +1</td>
<td>9 to 19</td>
<td>47 to 48</td>
<td>92</td>
<td>° C</td>
<td></td>
</tr>
<tr>
<td>19,4 (40,1)</td>
<td>9,5 (41,7)</td>
<td>8,6 (74,5)</td>
<td>6,0 (126)</td>
<td>DIN 51794</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Explosion limit (°) upper</td>
<td>415</td>
<td>383</td>
<td>293</td>
<td>258</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Autoignition temperature</td>
<td>384</td>
<td>347</td>
<td>292</td>
<td>234</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of evaporation at boiling point</td>
<td>950</td>
<td>655</td>
<td>504</td>
<td>332</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of polymerisation</td>
<td>22504</td>
<td>25476</td>
<td>29385</td>
<td>37555</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>2,01</td>
<td>1,97</td>
<td>1,98</td>
<td>1,97</td>
<td>kJ / kg</td>
<td></td>
</tr>
<tr>
<td>Specific heat of liquid at K 293</td>
<td>0,956</td>
<td>0,923</td>
<td>0,899</td>
<td>0,886</td>
<td>t / m³</td>
<td></td>
</tr>
<tr>
<td>Density of liquid at K 293</td>
<td>0,923</td>
<td>3,5</td>
<td>4,4</td>
<td>6,4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapour density (air = 1)</td>
<td>1,3 x 10¹</td>
<td>1,3 x 10¹</td>
<td>1,15 x 10¹</td>
<td>0,8 x 10¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coefficient of cubic expansion</td>
<td>1,402 to 1,404</td>
<td>1,404 to 1,419</td>
<td>1,415 to 1,418</td>
<td>1,434 to 1,437</td>
<td>DIN 51757</td>
<td></td>
</tr>
<tr>
<td>Refractive index nD at K 293</td>
<td>0,63</td>
<td>0,63</td>
<td>0,57</td>
<td>0,92</td>
<td>2,79</td>
<td>DIN 53169</td>
</tr>
<tr>
<td>Viscosity at K 273</td>
<td>0,63</td>
<td>0,72</td>
<td>1,28</td>
<td>2,79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface tension at K 293</td>
<td>0,63</td>
<td>0,49</td>
<td>0,57</td>
<td>0,92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility: ester in water</td>
<td>26000</td>
<td>15000</td>
<td>2000</td>
<td>9,6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>water in ester</td>
<td>22500</td>
<td>15000</td>
<td>7000</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>1,1x10⁰</td>
<td>2,1x10⁰</td>
<td>1,7x10⁰</td>
<td>2,8x10⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>kg / l</td>
<td>mPa.s</td>
<td>mg / l</td>
<td>pH / m</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.1 Polymerisation caused by overheating

The most frequent cause of an untimely polymerisation is overheating (e.g. by storing close to a heat source). The maximum temperature for storage of acrylic esters is 35°C. Higher temperatures may lead to a higher consumption rate of the stabiliser system (consisting of MeHQ and oxygen) and consequently to an untimely polymerisation.

4.1.2 Polymerisation caused by oxygen depletion

Acrylic esters must never be handled or stored under an inert atmosphere. The presence of oxygen is required for the stabiliser to function effectively. Dissolved oxygen converts carbon centered free radicals to oxygen centered radicals. The MeHQ works by trapping these oxygen centered radicals to stabilise the acrylic ester. A head space containing sufficient air should always be maintained above the monomer to ensure inhibitor effectiveness.

Dissolved oxygen takes part in the inhibition reaction and therefore is gradually consumed. The level of dissolved oxygen should periodically be replenished (see section 7). This can be accomplished by thoroughly aerating the liquid phase, (e.g. recirculation of the inventory in tanks or agitating drums by rotating).

NEVER USE AN INERT ATMOSPHERE ABOVE AN ACRYLIC ESTER.

Methyl acrylate and ethyl acrylate are flammable. Standard industry handling practice for non-acrylic monomer flammables is to use inert gas (nitrogen) for blowing and pigging of lines for pressure drop type level measurement devices, and for blanketing of tanks. However the MEHQ inhibitor used in acrylic esters requires the presence of dissolved oxygen in the monomer. It is recommended that the acrylic ester be kept in contact with an atmosphere containing 5 to 21 vol. percent oxygen.

In some applications (e.g. where tank vents are collected into a header for incineration) there may be safety concerns that prevent the use of air to blanket flammable acrylic esters. An appropriate safety analysis should be carried out, and applicable local regulations should be consulted.

The limiting oxygen concentration (LOC) is the minimum concentration of oxygen that will propagate a flame in a gas mixture. The LOC of methyl acrylate and ethyl acrylate are approximately 8.5 and 9.0 vol. percent, respectively.

To address flammability concerns while maintaining the necessary oxygen for inhibition, a mixture of air and nitrogen may be employed. An air-nitrogen mixing station can be designed to yield a gas containing a minimumum of 5 vol. percent oxygen. Equipment measurement tolerances must be carefully considered to ensure the operating range remains comfortably between the LOC and the minimum recommended oxygen concentration (5%). For example if analysis of the proposed mixing station design shows that the tolerance is ± 1.5%, then the setpoint of the system must be 6.5% in order to ensure that the oxygen concentration is always above 5 vol. percent. The design of the mixing station should be reviewed with local safety personnel to ensure that it meets the criterion for both protection from flammability of the material and for protection from unexpected polymerisation through all normal and emergency operations.

4.1.3. Polymerisation caused by Contamination

Good housekeeping must be exercised and special care must be taken to exclude all contaminants from a storage vessel. Many substances are known to readily undergo reactions with acrylic esters. The greatest hazard with respect to runaway polymerisations are materials capable of initiating them, such as peroxides, peroxide forming chemicals or azo-compounds (see also 4.1). Initiating radicals may also be formed under certain conditions from polyvalent heavy metal ions participating in redox reactions. Such metal ions include: copper, cobalt, nickel, chromium and iron. Nitric acid present in small amounts can also start polymerisation.

Tanks should be protected from mistakenly being charged with other materials or from back flow from other production vessels. This can be best achieved by using dedicated loading and unloading lines with proper identification.
Tanks, piping and transport vessels should be inspected periodically for polymer formation as the polymer can act as a seed for further polymerisation. Polymers of the esters are commonly soluble in the monomer.

A list of incompatible materials is indicated in Appendix.

4.2 Fire and Explosion Hazards

All acrylic esters with the exception of 2-ethylhexyl acrylate form readily ignitable vapours at ambient temperatures. The flash points and other flammability characteristics are listed in table 4. When oxygen is present above the LOC, ignition may occur in the presence of ignition sources. Beside common sources of ignition spark discharge from static electricity or improperly grounded and bonded vessels should be investigated.

**Table 4**

<table>
<thead>
<tr>
<th>Property</th>
<th>Methyl acrylate</th>
<th>Ethyl acrylate</th>
<th>Butyl acrylate</th>
<th>2-Ethylhexyl acrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point °C (closed cup)</td>
<td>-3 to -2</td>
<td>8 to 9</td>
<td>36 to 40</td>
<td>82 to 87</td>
</tr>
<tr>
<td>Flamable limits at 25°C in air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- lower limit (vol %)</td>
<td>2.5</td>
<td>1.1</td>
<td>1.3</td>
<td>0.7</td>
</tr>
<tr>
<td>- upper limit (vol %)</td>
<td>12.0</td>
<td>11.8</td>
<td>9.9</td>
<td>8.2</td>
</tr>
<tr>
<td>Expl. limit upp. °C</td>
<td>40.1</td>
<td>41.7</td>
<td>74.5</td>
<td>126</td>
</tr>
<tr>
<td>low. °C</td>
<td>-3.8</td>
<td>6.4</td>
<td>34.9</td>
<td>82</td>
</tr>
<tr>
<td>Autoign. temp. °C</td>
<td>415</td>
<td>371</td>
<td>293</td>
<td>258</td>
</tr>
<tr>
<td>Temp. class VDE</td>
<td>T2</td>
<td>T2</td>
<td>T3</td>
<td>T3</td>
</tr>
<tr>
<td>Electr. equipm. NEC</td>
<td>all</td>
<td>CLASS I; DIV.II; Group D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flammability VbF</td>
<td>A I</td>
<td>A I</td>
<td>A II</td>
<td>A III</td>
</tr>
<tr>
<td>Flammability NFPA 30</td>
<td>I B</td>
<td>I B</td>
<td>combustible</td>
<td>combustible</td>
</tr>
</tbody>
</table>

Acrylic esters flowing through or being discharged from a pipeline may generate static electricity. Hence, during transfer from one container into another these should be electrically interconnected (bonded) and properly grounded. Splashing into a tank should be avoided by the use of a dip tube. If mixing nozzles are used in storage tanks (see section 9.1), care should be taken to keep the nozzles always well below the liquid surface to avoid spraying.

All permanent storage tanks that contain acrylic esters with low flash points are required to be fitted with the legally obligatory fire protection equipment. Outlets to the atmosphere must be protected with flame arrestors and detonation traps. For detailed information see section 9.

Exhaust gases loaded with acrylic esters are best purified in a wet scrubber using ordinary caustic, aqueous organic amines or a mixture of both. For the final off gas purification an activated carbon cartridge can be used. The heat of absorption for all acrylic monomers on activated carbon is unusually high. Therefore if highly loaded exhaust gases are passed over activated carbon, ignition of the carbon bed may occur.

Active carbon cartridges must never be used for the removal of acrylic esters from exhaust gasses, unless the gasses are pre-treated in a wet scrubber. For the prevention of flame flashback into the tank, carbon cartridges must always be separated from the tank by a flame arrestor.

All esters are immiscible with water. Consequently water will not adequately extinguish a fire. However, if a fire occurs in or close to a tank farm containing acrylic monomers, tanks and pipes should be cooled by spraying with plenty of water in order to prevent monomers from polymerising. Small fires can be fought with carbon dioxide or dry chemical extinguishers. For larger fires, foam is suitable.
5 Health and Safety Factors

5.1 Toxicity

Acrylic esters may cause irritation to mammalian tissues and mucous membranes. Extended exposure of dermal tissue to liquid or high concentrations of vapours may result in an erythema. In rare cases blister formation has also been observed after extended exposure to liquid esters (For first aid recommendations see section 5.3). A skin sensitising effect in humans has been reported for most of the esters.

Inhalation of concentrated vapours and mist could produce moderate to severe irritation of the respiratory tract. High concentrations could also result in pulmonary oedema, while lower concentrations could produce nasal and throat irritation. Lachrymation from the eyes may also occur after inhalation. The vapours of the light esters have a narcotic effect and may result in drowsiness or, in severe cases, also in a loss of consciousness.

Table 5

<table>
<thead>
<tr>
<th>Toxicity</th>
<th>Acute oral, Rat LDS0 (mg/kg bw)</th>
<th>Inhalation, Rat LC 50, mg/l, 4h</th>
<th>Dermal, Rabbit LDS0 (mg/kg bw)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>765</td>
<td>5.7</td>
<td>1250</td>
<td>SIAR MA³</td>
</tr>
<tr>
<td>Ethyl</td>
<td>550-2000</td>
<td>5.9</td>
<td>1800 (rat 470)</td>
<td>IUCLID⁴</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>3143</td>
<td>10.3</td>
<td>2000-3024 (SIAR-BA)³</td>
<td></td>
</tr>
<tr>
<td>2-Ethylhexyl</td>
<td>4000 - 6000</td>
<td>²</td>
<td>14000</td>
<td></td>
</tr>
</tbody>
</table>

⁴ EU-Risk Assessment Draft of 25.04.2002
⁵ ECB-Iuclid-Dataset (2000)

Although ingestion is not an expected route of human exposure, swallowing of acrylic esters may cause severe irritations or burns of the mouth, throat, oesophagus, and stomach.

No serious health effects have been reported in humans exposed to single or repeated exposure at low concentrations of acrylic esters (for exposure threshold limits see sector 5.2). The data in table 5 reflect the toxicity.

5.2 Industrial Hygiene

Direct skin and eye contact with acrylic esters must be prevented. The current Occupational Exposure Limits OEL and Short Term Exposure Limits STEL are listed in the following table 6. Since exposure values may differ in different localities and are subject to change, check with the local authorities or with your environmental department for applicable national OEL values.

Table 6

<table>
<thead>
<tr>
<th></th>
<th>OEL (8hr TWA)</th>
<th>STEL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>Mg / m³</td>
</tr>
<tr>
<td>Methyl</td>
<td>5 - 10</td>
<td>18 - 35</td>
</tr>
<tr>
<td>Ethyl</td>
<td>5</td>
<td>21</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>2-Ethylhexyl</td>
<td>not established</td>
<td></td>
</tr>
</tbody>
</table>
Acrylic esters should only be handled in well aerated and ventilated places. If an exposure to concentrated vapours cannot be avoided (e.g. in accidents), self-contained breathing apparatus or air supply masks must be worn. Full face filter masks can be used when there is a low concentration of vapor. Care must be taken when using filter-type masks to ensure that their filter capacity is not exceeded for the intended time of use and expected concentration.

In areas where a release of acrylic esters is possible, eye protection, face shields, NEOPRENE rubber gloves, and rubber boots should be worn. A chemical suit with a self contained breathing apparatus is strongly recommended if larger spills or emissions have to be cleared. Appropriate protective clothing should be worn for work involving breaking or entering into a closed system containing acrylic esters. Due to the natural vapour pressure, the concentration of acrylic esters in closed rooms can far exceed the corresponding OELs.

If clothing or shoes have accidentally been contaminated with acrylic esters, they must be removed immediately. Contaminated leather shoes or other leather goods should be discarded.

For a timely and appropriate emergency response, it is advisable to provide complete sets of safety protection equipment near places where incidents with acrylic esters are possible.

5.3 First Aid

In order to minimise consequences of accidents, all personnel assigned to handle acrylic esters must be aware that prompt and appropriate response (see following sections) is essential. First aid must be rendered immediately. The installation of a sufficient number of emergency showers and eye washes are important for the proper management of incidents. The phone number to call for emergency medical services and all workplace specific emergency procedures should be available.

When providing first aid to a person who has been exposed to acrylates, the victim should be removed from the area to prevent further exposure. The type of exposure the person has experienced should be determined – eye or skin contact, inhalation or ingestion. If possible, do not leave an injured person alone. A co-worker should be instructed to call for help while assistance is being provided to the affected individual.

Following local regulations, if a worker working alone is exposed to acrylates, the worker should leave the area. After finding a co-worker and instructing them to call for help, the exposed worker should follow procedures to remove or dilute the contamination.

5.3.1 First Aid in case of eye contact

If acrylic esters enter the eyes, they must be cleaned with an eye wash with large amounts of lukewarm water for at least 15 minutes. The assistance of a helper is advised to make sure that all material is removed. The eyelids should be held wide open and away from the eyeballs. Immediate assistance of an eye specialist should be sought.

If a physician is not immediately available, the process of flushing the eyes with water should be continued for a second 15 minute period. Do not put any ointments or medications in a person’s eyes unless specifically instructed by a physician.

**DO NOT APPLY OIL OR OILY OINTMENTS UNLESS ORDERED BY A PHYSICIAN.**

5.3.2 First Aid in case of skin contact

In the event that skin contact with acrylic esters has occurred, all clothing should be completely removed. Washing with water under an emergency shower should be continued until all odour has disappeared from the skin.

The exposed individual should be evaluated by a physician as soon as possible due to the potential for serious harm. No ointments or medications should be applied to the skin without specific instruction from a physician.
ALL CONTAMINATED CLOTHING MUST BE APPROPRIATELY DE-CONTAMINATED PRIOR TO RE-USE. DO NOT TAKE CONTAMINATED ITEMS HOME FOR LAUNDERING! IF THE FACILITY IS NOT EQUIPPED TO DECONTAMINATE CLOTHING AND OTHER ITEMS, THEY SHOULD BE PROPERLY DISPOSED OF AND REPLACED. CONTAMINATED LEATHER ITEMS CANNOT BE ADEQUATELY DE-CONTAMINATED AND SHOULD BE DISCARDED.

5.3.3 First Aid in case of inhalation

If a person has suffered from inhalation of acrylic ester vapours, remove them at once from the contaminated area and make them lie down in a well ventilated area. They should remain there without moving. If the patient is unconscious, place them on their side in a stable position. Call a physician and ambulance immediately.

Suggestions to Physicians

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

In most exposures, administration of oxygen at atmospheric pressure has been found to be adequate. This is best accomplished by use of a face mask with a reservoir bag of the non-rebreathing type. Inhalation of pure oxygen (100 percent) should not exceed one hour of continuous treatment. After each hour, therapy may be interrupted. It may be reinstated as the clinical condition indicates. In the event of symptoms caused by exposure to acrylates, or in the case of a history of severe exposure, the patient may be treated with oxygen under 0.4 kPa (4 cm of water) exhalation pressure for one-half hour periods out of every hour. Treatment may be continued in this way until symptoms subside or other clinical indications for interruption appear. IT MAY NOT BE ADVISABLE TO ADMINISTER OXYGEN UNDER POSITIVE PRESSURE IN THE PRESENCE OF IMPENDING OR EXISTING CARDIOVASCULAR FAILURE.

5.3.4 First Aid in case of ingestion

Do not induce vomiting. Call a physician and ambulance immediately. Make the patient drink large amounts of water but advise that the amount should be restricted if vomiting occurs. Vomiting can potentially cause burns to the esophagus and other internal organs. Immediately contact local emergency medical services or the local poison control center for assistance. The exposed individual should be evaluated by a physician as soon as possible due to the potential for serious harm.
6. General Considerations for Transport and Storage

6.1 Temperature

A major concern during the storage of acrylic esters is high temperature. Temperatures above 35 °C, which could lead to a premature consumption of the inhibitor system, should be avoided. Ideally, acrylic esters should be stored at ambient temperatures. (see following section).

6.2 Duration of Storage

The inhibitor system, consisting of MeHQ and oxygen, is gradually consumed during storage. Oxygen therefore should periodically be replenished by agitating the monomer, thus bringing it into close contact with the air in the head space of the container. In storage tanks the appropriate oxygen concentration can best be maintained by regularly circulating the tank contents for a few hours every four weeks (see sect. 7.4.4). Although the dissolved oxygen is used up more quickly than the MeHQ, an analytical measurement of the inhibitor concentration is also recommended if the material is held for more than two months.

The consumption rate of inhibitor and oxygen depends mainly on the average storage temperature. However, the inhibition reaction (monomer plus oxygen) gradually generates increasing quantities of radical forming material. This may adversely alter the reactivity of the monomer in normal use. High concentrations of radical forming material may make it more difficult to polymerise the material. Provided the temperature of the material has not exceeded 35 °C and the concentration of inhibitor is correctly maintained, safe storage of 1 year can be expected.

Drums should be stored in a climate controlled and well ventilated warehouse. To minimise the likelihood of storing the material for too long, make sure that the storing procedure strictly follows the “first-in-first-out” principle. For storage periods over two months it is advisable to periodically rotate the drums, in order to replenish the dissolved oxygen content.

FOR PROPER HANDLING OF MATERIAL STORED LONGER THAN ITS STATED MAXIMUM STORAGE TIME, CALL YOUR SUPPLIER.
6.3 Labelling

Acrylic esters are shipped in bulk, ISO-containers and drums in compliance with regulations according to ADR/RID/IMDG/ GGVS/GGVE specifications (see following table 7). If small volumes are required, esters are often shipped in steel drums. Stainless steel IBC-containers are recommended for the transport of amounts up to 1 cubic metre.

<table>
<thead>
<tr>
<th>Classification / Labelling</th>
<th>Methyl acrylate</th>
<th>Ethyl acrylate</th>
<th>n-Butyl acrylate</th>
<th>2-Ethylhexyl acrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN Product No.</td>
<td>1919</td>
<td>1917</td>
<td>2348</td>
<td>-</td>
</tr>
<tr>
<td>Risk No.</td>
<td>339</td>
<td>339</td>
<td>39</td>
<td>-</td>
</tr>
<tr>
<td>LAND (ADR/RID/ GGVS/GGVE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class</td>
<td>3 / 3b</td>
<td>3 / 3b</td>
<td>3 / 31c</td>
<td>n.c.</td>
</tr>
<tr>
<td>AIR (ICAO/IATA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>n.c.</td>
</tr>
<tr>
<td>RIVER (ADN/ADNR)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class</td>
<td>3 / 3b</td>
<td>3 / 3b</td>
<td>3 / 31c</td>
<td>n.c.</td>
</tr>
<tr>
<td>SEA (IMDG/GGVSea)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class</td>
<td>3.2</td>
<td>3.2</td>
<td>3.3</td>
<td>n.c.</td>
</tr>
<tr>
<td>EC Labelling</td>
<td>Xi</td>
<td>Xi</td>
<td>Xi</td>
<td>Xi</td>
</tr>
</tbody>
</table>

If indoor storage facilities are not available, drums should never be placed in direct sun light. If drums are sheltered under tarpaulins, care must be exercised to provide adequate ventilation under the shelter. Otherwise considerable heat can develop from sun radiation. During long, hot weather periods it is advisable to aim a water spray on the surface of the shelter.
7. Bulk Storage Facilities and Accessories

7.1 General Considerations

Manufacturers of acrylic esters can provide information on special design features for the specific hazards of bulk storage. When planning a storage facility, care should be taken to minimize monomer volumes to minimize the consequences of an inadvertent polymerisation or fire.

The recommended maximum bulk storage temperature range is 35 °C. This maximum allows time to detect and react to an inadvertent polymerisation. Avoid heating systems that can generate high surface temperatures. **UNDER NO CIRCUMSTANCES SHOULD STEAM OR UNREGULATED ELECTRIC TRACING BE USED TO HEAT ACRYLIC ESTERS.** Localised high temperatures can quickly initiate polymerisation. Uncontrolled polymerisation can be violent and may result in serious injury and/or loss of property. Electrical heat tracing should not be used on piping systems (including pumps, valves and filters) or vessels in acrylic ester service unless it can be ensured that the resulting recommended maximum temperature of the acrylic ester cannot exceed 35 °C during heating.

Adequate inhibition is necessary to avoid polymerisation in a properly stored acrylic ester. The standard level of inhibitor in commercially available acrylic esters is 10-20 ppm MeHQ. In addition to the MeHQ, the presence of dissolved oxygen in the liquid is essential for stabilisation. Therefore, an atmosphere containing 5 to 21 vol.% of oxygen should be maintained above the acrylic ester. **NEVER USE AN INERT ATMOSPHERE.** Dissolved oxygen converts carbon centered radicals to oxygen centered radicals, which the MeHQ can trap to stabilise the acrylic ester (see Chapter 4.1).

Typically a 10% void volume is used in bulk storage vessels as a buffer against tank overflow. This also provides adequate oxygen containing gas to activate the MeHQ inhibitor.

Avoid condensation in vessel vent lines and nozzles. Condensed acrylic esters can quickly polymerise due to a lack of inhibitor. Polymerisation can lead to dangerous plugging of the pressure relief or vacuum relief vent system.

Take every precaution to keep acrylic esters free of contamination (e.g. by using dedicated equipment and lines). Trace contamination with an initiator can lead to a dangerous inadvertent polymerisation (see Chapter 4.1).

Never store or handle acrylic esters in a facility without first carefully reviewing the design of all vessels and accessories for potential hazards. **NEVER STORE ACRYLIC ESTERS IN A VESSEL IN WHICH STEAM CAN ACCIDENTALLY HEAT THE MATERIAL THROUGH A HEAT TRANSFER SURFACE OR BY DIRECT ADDITION TO THE VESSEL.** Storage in process vessels or in storage tanks designed for other chemicals can lead to unsafe conditions.

**ALL ACRYLIC ESTERS STORAGE VESSELS (INCLUDING CHARGE OR WEIGH TANKS) SHOULD HAVE A HIGH TEMPERATURE ALARM.** The purpose of this alarm is to detect an inadvertent polymerisation or the introduction of excessive heat from external sources. Properly located and maintained redundant temperature probes (minimum 2) connected to a high temperature alarm can provide early warning of potentially unsafe conditions and allow time for corrective actions to be taken.

**ALL ACRYLIC ESTERS PUMPS SHOULD BE PROTECTED FROM OVERHEATING.** If deadheaded, many types of pumps can quickly overheat and cause a violent polymerisation, which could result in serious injury and/or loss of property.

Periodically inspect vent nozzles and lines for polymer. Promptly remove any polymer found in the system. Polymer can cause plugging and may promote further polymerisation under some conditions. It is good practice not to leave stagnant lines or nozzles liquid-full for over 48 hours. Dissolved oxygen is slowly consumed and must be replenished by occasional circulation or clearing the lines with a gas containing 5 to 21 vol.% of oxygen. Depletion of oxygen can cause polymer formation and plugging.

Indoor acrylic esters storage facilities must be well ventilated to prevent local accumulation of vapors and their potential harmful effects on personnel.
7.2 Design Considerations

Some design considerations for bulk acrylic esters storage facilities and accessories are given in Chapters 7.2.1 through 7.2.6. It is recommended that fail-safe positioning of automated valves and emergency backup power for critical instrumentation be included in the design. Follow applicable local all codes and regulations.

A typical design for an outdoor tank installation is shown in the appendix to this brochure. A commentary is given in section 9.1. The special features of the design are derived from long-term experience and have been shown to be reliable. Any design should have the appropriate engineering, safety, and environmental review before implementing. For environmental reasons, tanks and pumps should always be positioned in a diked area. Contact your acrylic ester supplier for additional guidance.

7.2.1. Temperature Control of Bulk Storage Tanks and Accessories

All storage tanks located outdoors should be built in such a way that the temperature can be controlled under 35°C. This provides sufficient time for potential emergency response if the temperature increases due to a polymerisation or fire. It may be necessary to use a heat exchanger in order to provide cooling during warmer weather and/or to remove heat generated by pumps.

UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT ACRYLIC ESTERS.

THE DESIGN OF INDOOR BULK STORAGE FACILITIES AND ACCESSORIES MUST ADDRESS THE SPECIAL FIRE, HEALTH AND REACTIVITY HAZARDS THAT ARE A PART OF INDOOR STORAGE FACILITIES.

All storage tanks located indoors must be vented to the outside.

7.2.2. Pumps and Protection of Pumps from Overheating

It is suggested that reliable engineering safeguards, such as redundant instrument interlocks tested on a regular basis, be provided to prevent accidental overheating of acrylic ester pumps. OVERHEATING OF ACRYLIC ESTER PUMPS CAN CAUSE A VIOLENT POLYMERISATION, WHICH MAY RESULT IN SERIOUS INJURY AND/OR LOSS OF PROPERTY.

Some options to help protect pumps from overheating are given below:

- 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 temperature rise inside the pump (consider emergency response capabilities, see Chapter 11).
- A power monitor that senses a 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. Deadheading a centrifugal pump usually results in an immediate reduction in power consumption.
- 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 should be installed in order to provide redundant protection from pump overheating.

Other considerations associated with pumping acrylic esters are given below:

- Double mechanical seal and magnetic drive centrifugal pumps are commonly used for acrylic ester service. These pumps require instrument interlocks to prevent dangerous overheating in case deadheading occurs.
- 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.
- Seals and bearings in contact with acrylic ester should be flushed for adequate cooling and lubrication. High surface temperatures can cause polymer particles to form.
• Truck mounted pumps should not to be used for unloading acrylic ester because of the potential for contamination, leaks and overheating.

Some guidance related to environmental protection relevant to pumps is given in Chapter 7.2.6.

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

7.2.3. Detecting Unsafe Conditions Inside Bulk Storage Vessels

Storage tanks need to be inspected on a regular basis in order to prevent polymer from covering essential safety devices. It is highly recommended that all vessels used to store acrylic esters liquid have two independent temperature probes connected to a high temperature alarm. This includes storage tanks, check tanks, weigh vessels, and charge vessels. The two temperature probes should be located near the bottom of the vessel (preferably 90 to 180 degrees apart) and alarm in the control room in the event that either probe exceeds the high temperature set point. It is also suggested that both temperatures and rates of temperature change be monitored. These temperature probes and alarms are essential for confirming safe storage conditions and for emergency response to an inadvertent polymerisation (see Chapter 11.1.2). Careful monitoring of temperatures and rates of temperature change is critical if unsafe conditions occur inside of a vessel.

**EARLY DETECTION OF A HIGH TEMPERATURE INSIDE AN ACRYLIC ESTER VESSEL CAN FACILITATE TIMELY EMERGENCY RESPONSE TO A DANGEROUS INADVERTENT POLYMERISATION AND MAY HELP AVOID SERIOUS INJURY AND/OR LOSS OF PROPERTY.**

Circulating the vessel contents helps to prevent temperature variation within the vessel and thus will provide early warning if localised polymerisation occurs. Contact your supplier for additional guidance on temperature monitoring of vessels and related emergency response.

7.2.4. Avoiding Polymer Formation in Vent Nozzles and Lines

It is recommended that precautions be taken to minimise potential condensation of acrylic esters in vent nozzles and lines. Acrylic esters condensed from vapor do not contain MeHQ stabiliser and are prone to form polymer, which can plug critical pressure and vacuum relief lines.

Slope vent lines to drain condensed liquid back to a vessel when possible and provide liquid drains where stagnant liquid pockets may develop. Polymer formation is likely in stagnant pockets of uninhibited acrylic esters. Heating vent lines with regulated electric tracing systems may be advisable, depending on the acrylic ester and on the ambient temperature.

7.2.5. Indoor Acrylic Ester Storage Facilities

All local codes and regulations should be followed. The special risks associated with indoor facilities should be considered during the initial project safety, health and environmental review as well as in all subsequent reviews. In particular, the consequences of spill, fire, and inadvertent polymerisation should be carefully considered. Indoor acrylic ester storage facilities must be well ventilated to prevent local accumulation of vapors, which can have potential harmful effects on personnel. Note that the vapors from acrylic esters are heavier than air and may accumulate in low areas in the building. It is suggested that local exhaust systems be considered to supplement the general exhaust system and that adequate air change rates are ensured. It is recommended that all laboratories be provided with a sufficient number of properly designed exhaust hoods. All indoor bulk storage tanks should vent outside of the building.
7.2.6. Engineering Features for Environmental Protection

All local environmental regulations should be met. Spill containment helps protect public waterways and ground water. Dikes around storage tanks are used to contain spills. Properly designed dikes and flooring constructed of concrete which can hold the entire contents of the largest tank, are suggested as secondary containment. Spill containment for bulk unloading areas will reduce environmental risks. Concrete containment is suggested for bulk unloading areas. The use of dry disconnect fittings can reduce releases and may help avoid a spill if accidentally opened under pressure. Instrumentation to monitor the liquid level in bulk storage tanks is recommended to help prevent spills. See Chapter 7.2.11.

Vapor return lines are suggested for bulk unloading facilities to reduce emissions (see Chapter 7.2.9). If needed, scrubbers or thermal oxidation units can be used to control emissions. Local, state, and federal regulations may apply. Contact your supplier for additional guidance.

Magnetic drive and double mechanical seal centrifugal pumps as well as air-driven diaphragm type pumps can reduce fugitive emissions and the risk of spills. Double mechanical seals are commercially available using a liquid (such as a glycol) or a gas (such as oil free air) as the barrier fluid. Environmental protection should be considered in the selection of pumps.

7.2.7. Engineering Considerations for Fire Control

It is highly recommended that engineering safeguards be provided for reducing the risk of an inadvertent polymerisation inside of a bulk storage tank during a fire. AN UNCONTROLLED HEAT SOURCE, SUCH AS A POOL FIRE, CAN CAUSE A VIOLENT POLYMERISATION RESULTING IN SERIOUS INJURY AND/OR LOSS OF PROPERTY. See Chapter 11 on emergency response.

Water monitors are suggested to help control pool fires that could surround acrylic ester tanks and to cool acrylic ester containing equipment during a fire. Isolation with dike walls can be used to protect acrylic ester tanks from pool fires caused by other chemicals. Combustible chemicals that are not fully miscible in water can complicate fire control around an acrylic ester storage tank.

A foam system should be used to extinguish an acrylic ester fire (see Chapter 11.3).

A restabilisation (shortstopping) system can be installed to allow the quick addition of phenothiazine (PTZ) in the event of a fire. Refer to Chapter 11.1.3 on restabilisation. Acrylic esters containing PTZ are much less likely to polymerise violently during a fire.

7.2.8. Materials for Construction and Sealing in Acrylic Ester Service

Proper choice of materials of construction is important for safety, health, and protection of the environment. Some specific guidance for acrylic ester service is given below. Contact your supplier for further information.

- Preferred construction material for tanks and pipes is stainless steel (i.e. EN 58 C or H; DIN 1.4571 or 1.4541; US 304L, 316L or 321). Carbon steel is also acceptable although the formation of rust may be a problem with product quality (color). Iron has also been shown to be a weak polymerisation initiator. If carbon steel is to be used, special procedures should be used to prepare the tank for use. Contact your supplier.
- Preferred gaskets are made of PTFE, cross-linked EPDM, stainless steel with graphite coating or Kalrez®.

7.2.9. Venting of Bulk Storage Tanks

Follow all local codes and regulations.

It is recommended that vacuum and pressure relief valves be installed unless the tank has an open vent to the atmosphere. A combination pressure-vacuum relief valve, sometimes referred to as a conservation vent valve, is frequently employed to help minimize the multiplicity of equipment and nozzles. Routine inspections of the conservation vent system are recommended to ensure operability and to remove any polymer (see Chapter 7.2.4).

It is suggested that vapor return (closed loop loading) lines be installed to significantly reduce emissions during unloading or loading of transport vessels such as rail cars or tank trucks. These lines should be kept free of polymer and the vent conservation valves correctly adjusted to contain most of the vapors during unloading and loading.
IT IS ESSENTIAL THAT INCOMPATIBLE CHEMICALS CAN NOT ENTER AN ACRYLIC ESTER STORAGE TANK THROUGH THE VENT SYSTEM.

Flame arrestors are recommended for acrylic ester storage tanks. An integrated flame arrestor is mandatory for all class A I and A II monomers. Precautions should be taken to keep flame arrestors free of polymer fouling (regular inspections recommended).

Storage tanks installed indoors require venting to the outside of the building.

7.2.10. Emergency Venting of Bulk Storage Tanks

There is no known accurate or simple method for the appropriate sizing of over pressure relief devices in a "worst-case" acrylic ester runaway scenario. The runaway polymerisation is an exothermic reaction in which information about worst-case temperature rise over time can be gathered through calorimetry studies. This information can be used to estimate energy generation, which in turn can be used to estimate vapor generation. It has been found that the temperature rise over time in a runaway polymerisation is minimised at lower reaction pressures. Consequently tanks designed with a low design pressure are recommended. Although no detailed information on runaway reactions in full sized tanks is available, weak seam or frangible roof designs on tanks with low height to diameter ratios are believed to provide best protection from a tank bursting in a worst-case incident.

For the natural breathing of the tank, a conservation valve should always be installed. Various designs such as weight loaded pressure pallet valves or breathing valves with flexible diaphragms are commercially available. An integrated flame arrestor is mandatory for all class A I and A II monomers. Acrylic ester vapours frequently condense on cold surfaces. The condensate may polymerise due to the lack of inhibitor. Consequently mechanical pressure relief devices and flame arrestors should periodically be checked for polymer. It is also recommended that these systems be electric heat traced with regulation in order to reduce condensation.

See Chapters 4.1 on Polymerisation and 11.1.3 on Restabilisation.

7.2.11. Other Bulk Storage Tank Accessories

Bulk storage tanks should have either a dip tube or a side entry nozzle for unloading and circulating the acrylic ester. Dip tubes are normally tack welded to the bottom and guided along the walls to assure static grounding and mechanical stability. They should have an antisiphon hole (ca. 5 mm) near the top, pointed towards the wall of the tank. Mixing during recirculation can be improved by locating the fill pipe 180° from the tank outlet. If entry nozzles are equipped with an eductor, the nozzle should always be well submerged when in use to avoid the possibility of forming a stable aerosol and ignition from static charge development. SUBMERGED NOZZLES AND PIPES CAN PLUG IF NOT FREQUENTLY UTILISED.

Level monitoring instrumentation is recommended to avoid spills when filling a storage tank and to avoid the problems associated with eductors. A minimum void volume of about 10 % of the oxygen containing blanket gas should be maintained above the liquid. It is recommended that the level monitoring instrumentation include a device which alarms if the tank is filled above or emptied below a safe level. The tanks should be equipped with a high-high level switch, which shuts off any inlet pump (unloading pump) before a potential spill. If mixing eductors are used, the tanks should also be equipped with a low-low level switch which stops circulation before the level drops below the eductor. If a differential pressure level indicator (bubbler type) is installed, a gas containing 5 to 21 vol.% of oxygen must be used. Dry, oil-free air is recommended for this service.

Safety showers and eye bath stations should be installed in the unloading and storage tank areas. Take precautions to prevent freezing in these stations as dictated by the local climate.

Pump glands, flanged fittings and valve stems should always be provided with splash collars if not insulated.
8. Equipment Preparation and Cleaning

8.1. General considerations

The hazardous nature of equipment preparation and cleaning requires that a qualified multifunctional team plan each step of the job in detail and consider all possible hazards. This team should ensure that stepwise safe work procedures are written which clarify hazards, preventive measures and personal protective equipment to be worn at each step. Equipment preparation and cleaning should be done under the direction of trained personnel who are familiar with the written stepwise safe work procedures. All involved personnel should understand the potential hazards pertaining to the job before work is initiated.

8.2. Commissioning and decommissioning of tanks

If information is needed, contact your supplier.

9. Safe Transport of Acrylic Esters

9.1. Personal protective equipment for loading, unloading and handling

Industrial hygiene exposure limits should be considered when selecting proper respiratory protection. Full protective clothing should be considered as proposed by the suppliers following the local regulations. Contact lenses substantially increase the risk of damage to eyes and, if your policies permit, should only be worn with special precautions. Full eye protection should include plastic shields with forehead protection in addition to chemical splash goggles.

9.2. General considerations

The following are general considerations that apply to all modes of transportation for acrylic esters. Also see Chapter 4 for Potential Hazards:

- Acrylic esters must be stored under an atmosphere containing 5 up to 21 vol. % of oxygen. The MeHQ inhibitor is not effective in the absence of oxygen.
- Do not use pure nitrogen or any other inert gas for sparging, blowing lines, or blanketing. Pure nitrogen or other oxygen-free gas could reduce the dissolved oxygen to a dangerously low level where the effectiveness of the inhibitor could be greatly reduced.
- Cleanliness is essential. All containers should be free of contamination.
- Avoid overheating of acrylic esters. **UNDER NO CIRCUMSTANCES SHOULD STEAM BE USED TO HEAT ACRYLIC ESTERS.** It should be ensured that the resulting maximum product temperature cannot exceed 35 °C.
- Most acrylic esters are classified as "Flammable" as defined in the transport regulations. As such, they must be packed in specific containers when shipped.
- EBAM suppliers adhere to all regulations concerning free air space in filled containers. This corresponds to a minimum void space of 5 % at 25 °C.
- Retained samples should be stored for no more than one year in a cool dark place. Amber glass bottles are recommended for handling and storing small amounts of acrylic esters.

9.3. Transportation Incidents - Immediate actions

If a shipping container (rail car, tank truck, drum, intermediate bulk container (IBC)) or its contents becomes damaged so that delivery cannot proceed safely, every effort should be made to move the container where it will not endanger traffic or property. If possible move the container to a vacant area away from populated areas. The local police and fire departments should be notified and the public should be restricted from the area. Follow precautions stipulated in the supplier’s MSDS for acrylic esters. See Chapter 11 on Emergency Response for additional information.
For further technical assistance consult the supplier immediately by calling the following telephone numbers.

<table>
<thead>
<tr>
<th>Company</th>
<th>Phone Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARKEMA</td>
<td>+33 (0) 3 879 38500</td>
</tr>
<tr>
<td>BASF SE</td>
<td>+49 (0) 180 2273 112</td>
</tr>
<tr>
<td>DOW Europe GmbH</td>
<td>+31 (0) 115 694 982</td>
</tr>
<tr>
<td>HEXION Specialty Chemicals, a.s.</td>
<td>+420 352 614 222</td>
</tr>
<tr>
<td>Rohm and Haas Europe Sarl</td>
<td>+33 (0) 1 4000.5045</td>
</tr>
<tr>
<td>Evonik Stockhausen</td>
<td>+49 (0) 2365 49 2232</td>
</tr>
<tr>
<td>SASOL Chemie GmbH &amp; Co KG</td>
<td>+44 (0) 208 762 8322</td>
</tr>
</tbody>
</table>

9.4. Bulk transport by road and rail

The bulk transport of acrylic esters, either by tank truck, rail car or iso container is authorized by ADR/RID and IMDG. Please consult these and/or local regulations for complete and up to date specifications and labeling requirements. The transport vessel should be constructed of stainless steel (see also Chapter 7.2.8.). In some climates it should be insulated in order to maintain the product temperature below 35°C.

9.4.1. Information for the Haulier

The haulier is responsible for providing transport units that meet all guidelines for safe transport of acrylic ester and proper product temperature during shipping. The temperature of the empty vessel should be less than 35°C before loading with an acrylic ester. **TEMPERATURES OF 40°C OR HIGHER CAN BE HAZARDOUS AND SHOULD BE IMMEDIATELY INVESTIGATED.** Drivers should be thoroughly trained about the hazards of acrylic esters. To ensure reliable operation, the temperatures of product should be monitored. In transit, the driver should log the temperature of the acrylic ester once every 8 hours until the delivery is made. The customer should be shown this log at the time of delivery. **IF AT ANY TIME THE TEMPERATURE OF THE ACRYLIC ESTER REACHES 40°C OR ABOVE, IMMEDIATELY CONTACT YOUR SUPPLIER (see Chapter 9.3.).**

High temperatures can be a warning sign of a possible inadvertent polymerisation. High temperatures can also cause an inadvertent polymerisation and must be taken seriously. The vessel should be isolated as dictated by the circumstances and conditions at the time. Also see Chapter 4 on Instability and Reactivity Hazards and Chapter 11 on Emergency Response for more details.

If transport vessels dedicated to each specific monomer are not used, a certificate of cleanliness indicating the previous cargo must be presented before starting the loading operation. See Chapters 10.4. and 12.1.

9.4.2 Unloading

The following procedures are suggested to reduce the risks during the unloading of acrylic esters. The contents of the vessel must be positively identified before they are transferred. If sampling is required, refer to site specific procedures. Continuous monitoring of the entire unloading process is appropriate. Acrylic esters are flammable liquids and should be handled accordingly.

An emergency shower and eye wash station should be directly accessible from the unloading area. The emergency shower and eye wash station should be tested periodically to ensure that they function properly. Personal protective equipment should be worn while sampling or making any connections.

Proper equipment should be used to protect against spills. It is preferable that truck unloading facilities be level and paved. They should be located such that the truck can easily and safely be manoeuvred. A place should be provided with a truck pad suitable to collect spillages for salvage or appropriate disposal. Where access to the top of the container is needed, the site should be equipped with stairs and a platform. An electrical grounding cable is required and must be attached to the transport vessel while loading or unloading the container. The piping for unloading should be on continuous circulation or arranged so the acrylic esters will drain toward the storage tank when transfer is stopped. Dry disconnect couplings are recommended to be provided on the unloading hose to ensure that a possible spill will be very limited in the event of a hose break. The pump glands, flanged fittings and valve stems should be provided with splash collars in cases where personnel could be exposed to major acrylic ester leaks or sprays.
9.4.2.1. Unloading Trucks and Iso Containers

The suggested unloading procedure is by pumping with a closed loop (vapour balance) system in which the vapours are returned to the vessel. If this system is not possible, the vapors should be sent to a scrubber or incinerator.

1. Spot the transport unit and set wheel chocks. The engine should be stopped and the emergency breaks applied during unloading.

2. Positively identify acrylic ester. Before unloading, inspect the vessel that it is not damaged or leaking. Compare the labels and the vessel identification number to ensure that they are identical to the transport documents.

3. The transport unit must be properly grounded before proceeding with any other operation.

4. **IF THE TEMPERATURE OF THE ACRYLIC ESTER IS ABOVE 40 °C, IMMEDIATELY CONTACT YOUR SUPPLIER.**

5. Verify that the receiving vessel will hold the entire contents of the tank truck or iso container.

6. Connect the vapour hose and open the valves to equalise pressure.

7. Remove the protection cap of the coupling.

8. Connect the liquid line and open the external valve.

9. Open the internal valve.

10. Start the pump. Once the flow has started, continue to monitor the vapour return line gauge to confirm the flow and to avoid pulling a vacuum that may implode the vessel.

11. When the vessel is empty, shut off the pump and close all liquid and vapour valves.

12. Drain and disconnect the hoses and replace the caps.

13. Leave the labels in place (according to the ADR/RID or IMDG guidelines).

14. Disconnect the earthing cables and remove the wheel chocks.

15. Verify that the vessel is empty.

If the vessel cannot be emptied for whatever reason, contact your supplier immediately.

9.4.3.2 Unloading Rail Cars

The suggested unloading procedure is by pumping with a closed loop (vapour balance) system in which the vapours are returned to the vessel, or sending the vapors to a scrubber or incinerator.

1. Spot the rail car and set wheel chocks.

2. Positively identify acrylic ester. Before unloading, inspect the rail car that it is not damaged or leaking. Compare the labels and the rail car identification number to ensure that they are identical to the transport documents.

3. The rail car must be properly grounded before proceeding with any other operation.

4. **IF THE TEMPERATURE OF THE ACRYLIC ESTER IS ABOVE 40 °C, IMMEDIATELY CONTACT YOUR SUPPLIER.**
5. Verify that the receiving vessel will hold the entire contents of the rail car.

6. Connect the vapour hose and open the valves to equalise pressure.

7. Remove the protection cap of the coupling.

8. Connect the liquid line and open the external valve.

9. Open the internal valve.

10. Start the pump. Once the flow has started, continue to monitor the vapour return line gauge to confirm the flow and to avoid pulling a vacuum that may implode the rail car.

11. When the rail car is empty, shut off the pump and close all liquid and vapour valves.

12. Drain and disconnect the hoses and replace the caps.

13. Leave the labels in place (according to the ADR/RID guidelines).

14. Disconnect the earthing cables and remove the wheel chocks.

15. Verify that the rail car is empty. If the vessel cannot be emptied for whatever reason, contact immediately your supplier.

9.4.2.3 Unloading Vessels with Pressure

It is not recommended to unload vessels by using pressurised gas. Your supplier should be contacted before this procedure is used.

9.5. Drums and intermediate bulk containers

The use of drums or IBC’s for transport of acrylic ester is authorised by the ADR/RID/IMDG regulations.

Drums made out of steel with an epoxy-phenolic internal coating are suitable for all acrylic esters. Drums made solely out of carbon steel may affect the product quality. Drums made of self-supporting high-density polyethylene cannot be used for the low boiling, highly flammable acrylic esters (methyl acrylate and ethyl acrylate) because of risk of electrostatic discharge.

IBC’s should be made of stainless steel unless they are equipped in such a way that no electrostatic discharge can take place during storage and unloading of the IBC.

Drums and IBC’s should be labeled properly.

9.5.1. Information for the Haulier

Avoid sources of heat, sparks, or flame. Acrylic esters should be shipped at temperatures below 35 °C.

Bulging or leaking drums with blistered paint may indicate polymerisation.

**IF POLYMERISATION IS SUSPECTED, IMMEDIATELY CONTACT YOUR SUPPLIER.** Also see Chapter 4 Potential Hazards and Chapter 11 Emergency Response for more details.
9.5.2. Storage of Drums and Intermediate Bulk Containers

Acrylic esters are normally inhibited with 10 to 20 ppm of MeHQ to prevent polymerisation. The three most important considerations in shipping and handling acrylic esters are to:

- **AVOID EXPOSURE TO ELEVATED TEMPERATURES,**
- **AVOID CONTAMINATION,** AND
- **USE AN OXYGEN CONTAINING BLANKET GAS.**

Acrylic esters should be kept below 35 °C. Do not store in direct sunlight.

Contamination can cause an uncontrolled polymerisation which may result in violent rupture of the container, fire, serious damage to the surroundings and significant environmental impact.

The presence of oxygen is required for the inhibitor (MeHQ) to be effective. Lack of oxygen can cause an uncontrolled polymerisation.

Re-use drums or IBC’s only if thoroughly cleaned or in dedicated service.

Steel drums with liners should be inspected periodically. Migration or penetration of acrylic esters vapors through the liner may cause polymerisation.

Please see Chapter 4 for additional information on potential hazards.

**WITH ACRYLIC ESTERS, NEVER USE STEAM OR ELECTRICAL HEATING, AS THIS CAN RESULT IN UNCONTROLLED POLYMERISATION.**

9.5.3. Emptying of Drums and Intermediate Bulk Containers

Acrylic esters are flammable liquids and should be handled accordingly. The contents of the drums and IBC’s should be positively identified before it is transferred. The following steps outline procedures for safely emptying drums and IBC’s:

1. Drums and IBC’s must be electrically grounded before starting and during the entire operation. A static-free dippipe or flexible stainless steel hose should be used to drain the acrylic ester.

2. Drums, IBC’s and fittings should never be struck with tools or other hard objects which may cause sparks.

3. Before removing plugs from acrylic ester drums or IBC’s, locate the nearest emergency safety shower and eye wash station and put on personal protective equipment.

4. The preferred safe method for emptying drums and IBC’s is by pumping. If drums or IBC’s are emptied by gravity, the valves should be self-closing. Do not use pressure to displace drums or IBC contents.

5. Provide adequate vacuum breaking to prevent collapse of the drums or IBC’s during emptying.
10. Environmental Considerations

10.1. Waste Disposal

State laws and local regulations governing waste disposal make it essential for producers, suppliers, haulers and users of acrylic esters to be fully aware of viable options for the ultimate disposal of materials containing acrylic esters. Materials to be disposed of may be residues from production or cleaning operations as well as waste material from spills.

If a biological treatment plant is available, minor amounts of monomers may be sparingly diluted with water and allowed to enter the treatment system. However, acrylic esters may be toxic to the system if the bacteria have not been conditioned properly to this material. Accordingly, the initial feed rate should be low with a stepwise increase if a significant amount is to be fed into the biological treatment purification. Due to the low odour threshold of most acrylic monomers, sending material to an open waste treatment system may cause odour problems. As acrylic esters are low to moderately toxic to fish, aquatic invertebrates and algae, biological treatment is necessary and spillages into surface waters and public sewers must be avoided.

Solid and liquid waste materials containing acrylic esters can be disposed of by incineration. Disposal in landfills must be thoroughly checked with the authorities.

For disposing of waste materials originating from a laboratory or for retained samples, great care must be exercised to keep the monomer separated from incompatible materials (see Chapter 12.1.) such as peroxides, which may initiate polymerisations.

10.2. Spill and Leak Control

Small spills, up to 5 litres, can suitably be absorbed in commercially available clean-up-kits (infusorial earth). If a waste water sewer is close by, the spill can also be washed down with water provided that it is not a storm-sewer or ditch which is routed to surface waters.

Large spills should be contained, if possible, within a diked area. A temporary dike can be arranged by stacking sand bags or similar devices. Avoid run-off into storm sewers routed to public waters. If possible, the material should be recovered in appropriate containers for re-use or disposed of, using explosion proof equipment. During all handling operations of large spills a chemical suit with self-contained or air-supplied breathing device must be worn.

In the event of accidental spillage of acrylic esters to surface water or to a municipal sewer system, the pollution control agencies must be promptly notified.

10.3. Air Emissions

Waste removed from gaseous plant discharges must be disposed of in conformity with air pollution control regulations.

The best way to avoid emissions is to eliminate those resulting from displaced gases from loading and unloading operations. In most cases this can be accomplished by back venting through a vapour return line. It should be considered good manufacturing practice in all storage facilities and (un-)loading installations. In order to properly use this system, the vent system must be separate from other systems to stop the contamination of acrylic esters.

Exhaust gases loaded with acrylic esters originating from production should be cleaned prior to being emitted into the atmosphere. The exhaust gas can be incinerated in a flare if one is within a reasonable distance.

A low cost alternative to incineration is a purification tower operated with an alkaline absorbant. Absorption is dramatically enhanced by the addition of non-volatile amines. Acrylic esters can readily be washed out from gasses and disposed of by either a biological treatment plant or by incineration. As an option it should also be considered to recycle the alkali acrylate in a production process.
The dimensional design for an appropriate tower depends on the flow rate of the gas. An approved design example with a corresponding drawing is suggested in Chapter 12.3.

10.4. Cleaning of Transport Vessels

10.4.1. Road Tanker

Road tankers in dedicated service for acrylic esters may develop a gradual growth of polymer on walls and armatures. If polymer has formed, it may possibly act as a seed for further polymerisation. Polymer particles may also adversely affect the quality.

It is therefore recommended to periodically clean containers thoroughly. The most effective way is to blast the interior of the tank first with cold water and then with hot water. The off-gases during the cleaning process should be vented through a scrubber or incinerated.

Cleaning has to be carried out in cleaning stations recommended by the European Federation of Tank Cleaning Organisations (EFTCO). A European Cleaning Certificate will be issued at these cleaning stations.

10.4.2. Used Drums

Material remaining in drums is a potential threat to the health of humans handling the drums afterwards. It should be considered as a rule of good housekeeping practice to thoroughly rinse, wash and dry emptied drums prior to being reused or discarded.
11. Emergency Response

Signs of an emergency involving acrylic esters often include increased temperatures (due to external heating or a polymerisation exotherm), venting of the container or container deformation. The proper initial action if there is an emergency during transport or in a user’s tank or drums is to call immediately your supplier (see Chapter 9.3.) and facilitate the establishment of communications between the personnel at the emergency site and the supplier’s emergency response team.

Users of acrylic esters should develop written emergency plans for acrylic esters spills, fires, exotherms and incipient polymerisations. These plans should focus on clearly identifying the features that categorise an event as an emergency, what should be done to secure the emergency site and immediate actions to mitigate the danger. A very important feature of the plan should be early notification of the incident so that the supplier can quickly provide expertise in helping to manage the incident.

11.1. Detection and response to incipient polymerisation in a storage tank

If a system is installed and operated with all of the preventative measures recommended in this brochure and required by prudent engineering practice, the chances of experiencing an inadvertent polymerisation are minimised. However, in the case of unforeseen events which might lead to polymerisation in a storage tank, it is necessary to detect such an event in a timely manner to avoid, stop or mitigate polymerisation. An option to provide additional protection from these unforeseen events is the use of a restabilisation (shortstop) system. This subsection deals with the operation of such an optional restabilisation system.

11.1.1 Credible Initiation Scenarios

The only quantitatively definable scenario studied kinetically for incipient runaway acrylic ester polymerisations involve external heating of the acrylic esters. Two other possible causes of acrylic esters runaways are removal of the dissolved oxygen from the monomer and chemical contamination.

If the monomer is purged with an inert gas (e.g., nitrogen or fuel gas) and the dissolved oxygen is removed, the MeHQ inhibitor becomes ineffective and polymerisation will ultimately occur. The length of the induction period until polymerisation occurs and the maximum rate of polymerisation are unpredictable because they depend on the previous storage history of the acrylic esters. If inert purging is known to have occurred, the acrylic esters should be sparged with a gas containing 5 to 21 vol. % of oxygen as soon as possible. For protection against ignition of the material, preference should be given to a mixture of air and nitrogen, thus limiting the oxygen concentration below the LOC corresponding to the specific ester.

The scope of a contamination scenario is very difficult to pre-define since the identity and concentration of the contaminant are unpredictable. However, it is recommended that any mischarge of chemical to a vessel be treated as a contamination that could cause a runaway polymerisation. The supplier should be immediately informed of the quantity and identity of the material that was mischarged. If a restabilisation (shortstop) system is available, it should be immediately activated. If such contamination has occurred without the knowledge of responsible personnel, the restabilisation (shortstop) system should be activated due to signs of the polymerisation exotherm.

11.1.2. Polymerisation Detection

Acrylate esters have the potential to polymerise very rapidly, generating a large amount of heat. A temperature rise that cannot be related to an external heat source should be considered an indication of a runaway polymerisation. In that event, exercise caution, but if a sample can be safely acquired, it can be used to test for the presence of soluble polymer to confirm polymerisation. While presence of soluble polymer confirms an ongoing polymerisation, inconsistent sampling can give a false negative result that does not prove anything until all the other indicators (may include multiple samples) indicate there is no polymerisation. To test for polymer in the monomer, add 20 ml of the monomer to 80 ml of water-free methanol. The polymer is insoluble in the methanol and the mixture will be cloudy if there is any polymer present.
Occasionally on the plant scale, uncontrolled acrylate ester polymerisations proceed slowly. Therefore, simple temperature rise may indicate an ongoing polymerisation. In the case of a slow temperature rise and with note of the caution below, the presence of soluble polymer in the monomer is one way to verify whether a polymerisation is underway before temperature extremes are reached.

**CAUTION: EVEN SLOW POLYMERISATION HAS THE POTENTIAL TO ACCELERATE INTO A RUNAWAY REACTION. IF THE TEMPERATURE RISES ABOVE 45°C OR THE RATE OF RISE IS GREATER THAN 2°C/HOUR, AND NO SOURCE OF EXTERNAL HEAT HAS BEEN IDENTIFIED, THIS SHOULD BE CONSIDERED AS THE ONSET OF POLYMERISATION. IF THE TEMPERATURE RISES AT A RATE GREATER THAN 5°C/HOUR OR THE TEMPERATURE REACHES 50°C, THE SITUATION IS CRITICAL.**

11.1.3. Restabilisation (Shortstopping)

Successful restabilisation of acrylic esters requires a timely response to detection of a significant temperature increase. The lack of a timely response may result in the onset of polymerisation leading to accelerated temperature and pressure rises. The quantitative relationships between rate of temperature rise, instantaneous temperature, and the time remaining until runaway occurs (for thermal initiation) have been correlated in kinetic studies. These results lead to the restabilisation system activation criteria given in 11.1.3.3. Due to the large number of possible contaminants and concentrations of those contaminants, these criteria **MAY NOT** apply if the cause of the polymerisation is contamination.

11.1.3.1. Restabilisation (Shortstop) Inhibitor

Experimental evidence leads to the recommendation of phenothiazine (PTZ) as the preferred shortstop agent. While addition of PTZ has worked in most cases, there is no assurance that it will always be effective. Obvious exceptions are contamination of acrylic esters with gross amounts of a polymerisation initiator or a delay in activation of the shortstop system. Phenothiazine is a solid, and for ease of mixing and addition, it should be added to the vessel as a solution in a compatible solvent. While the addition of PTZ will make the material unusable for normal applications, it may be reprocessed by your supplier.

11.1.3.2. Restabilisation (Shortstop) Inhibitor Solvent

Contact your supplier for recommendations for solvents and for proper handling of shortstop solutions. The following criteria are recommended for the selection of a solvent for the PTZ shortstop inhibitor:

- It should be miscible with the acrylic ester.
- It should be a good solvent for PTZ (preferably at least 6 wt % PTZ solubility at the lowest anticipated ambient temperature).
- It should not be viscous at low ambient temperatures.
- It should not promote polymerisation and should be inert to the system.
- It should not be highly toxic.
- It should not worsen any potential fugitive emission problem resulting from the emergency.
- (Optional) If successfully shortstopped, the acrylic esters containing the solvent should be capable of being repurified.

The PTZ shortstop solution should be as highly concentrated as possible to minimise its volume so that it can be delivered by pressurised gas or pumped into the system in as short a time as possible. The final concentration of PTZ in the acrylic ester to be shortstopped should be in the range of 200 to 1000 ppm. However, in the case of contamination, restabilisation may not be possible at any concentration of PTZ, depending on the nature and concentration of the contaminant.
11.1.3.3. Activation Criteria for Restabilisation (Shortstop) Systems

It is recommended that the restabilisation (shortstop) system be immediately activated if any of the following criteria are satisfied:

- A temperature rise of greater than 5°C/hour has been detected without external cause.
- The temperature in the liquid has reached 50°C.
- There is a fire near the acrylic ester tank.
- A known polymerisation initiator has been added to the acrylic ester.

These criteria have been chosen to ensure adequate time for the restabilizing agent to be fed to and dispersed in the tank contents. Lower temperatures or temperature increases than stated above may indicate an on-going polymerisation and still should be a cause for concern.

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 polymerisation. The lowest practical temperature or temperature rise should be used as a call for investigation.

Manual activation of the shortstop system is preferred for sites with continuous manning of personnel; otherwise automatic activation of shortstop system should be used. In any case, the shortstop system should be activated if the criteria specified above are met.

UNDER NO CIRCUMSTANCES SHOULD ANYONE NOT TRAINED IN THE APPROPRIATE EMERGENCY RESPONSE TECHNIQUES APPROACH A TANK IN WHICH THE CONTENTS HAVE REACHED 50°C. AT 60 °C ALL PERSONNEL SHOULD BE EVACUATED by THE LOCAL AUTHORITIES.

11.1.3.4. Mixing of Restabilisation (Shortstop) Inhibitor

It is possible to quickly bring the concentration of the shortstop inhibitor in the tank to effective levels by circulating the contents with a pump and/or by injecting a gas. If a pump is used to mix shortstop solution, the shutdown instrumentation must be designed to operate under emergency conditions (loss of power, instrument air, etc.). The use of eductor tubes on the tank inlet(s) or a gas lift can reduce the time required to mix the shortstop solution with the tank contents.

An important factor in the design and installation of the shortstop inhibitor system is the specific tank farm layout. The number of acrylic ester tanks, the location of diked walls and the types of chemicals within the diked areas should all be considered when planning a shortstop storage and distribution system. The shortstop system should be capable of distributing adequate inhibitor to all the acrylic ester tanks which could be involved in a given incident. For multiple tank protection, the options include a single inhibitor tank with controlled metering, separate dedicated inhibitor tanks and mobile inhibitor tanks. Your supplier can provide further details.

Another consideration is the location of the inhibitor tank(s) and how their contents will be delivered to the storage tanks. If the tanks are at ground level and far from the acrylic ester storage tanks, pump(s) may be necessary to transfer the PTZ solution from the inhibitor tank to the storage tank. Alternatively, the inhibitor tank(s) may be located in elevated positions near the storage tanks, with the inhibitor solution added to the storage tank’s recirculation line by pressure or by gravity flow. These options are best examined by plant personnel who will be most familiar with the specific tank farm layout. In case of using electrically driven pumps to feed the inhibitor solution to the storage facility, an electric energy backup system should be available.

11.1.3.5. Restabilisation (Shortstop) Systems

Contact your suppliers about design of restabilisation (shortstop) systems.
11.2. Spills

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

More information on spills is given in Chapter 10.2.

11.3. Fires

Acrylic esters are flammable liquids with flash points ranging from below 0°C to greater than 80°C. Under the recommended storage conditions, methyl- and ethyl acrylate are a highly significant fire risk because their temperatures can be well above their flash point.

In the event that the acrylic ester tank has caught fire, the first step should be to add a restabilisation (shortstop) agent as quickly as possible. This will help to prevent a runaway polymerisation from occurring, assuming that this was not the cause of the fire. Please note that water should not be added into a tank of burning acrylic ester. This is because water is not miscible with acrylic esters and all esters have a liquid density lower than water. Instead, foam should be used to extinguish the fire. After the fire is extinguished, continue to monitor the temperature of the storage tank for at least 48 hours to verify that the temperature is not rising and the tank is stabilised.

All acrylic esters are reactive materials which can polymerise if exposed to high temperatures. Therefore it is critical that any emergency plan contains measures to closely monitor the temperature of acrylic ester storage tanks in fire situations and that emergency response personnel are prepared to provide cooling to the storage tank. Incident commanders, fire fighters, and emergency response personnel must be trained on the polymerisation hazards of acrylic esters in order to determine the proper response in an emergency.

An acrylic ester storage tank fire or a fire in the vicinity of an acrylic ester storage tank is a very dangerous situation. If the acrylic ester reaches elevated temperatures the liquid could polymerise resulting in a violent reaction, evolving considerable heat and pressure and ejecting hot vapor, monomers and polymers. Therefore it is necessary to closely monitor the temperature of the ester during a fire situation. Quick response is essential for controlling and preventing escalation of the situation.

In the event of a severe fire with or near acrylic ester storage facilities, when the liquid temperature reaches 50°C it is necessary to evacuate all non-essential personnel to a safe distance from the tank or the buffer vessel because of the risk of a runaway polymerisation.

At 60°C ALL personnel should be evacuated based on local evacuation plans.

In the event of a fire in the immediate vicinity of an acrylic ester storage tank, apply water spray (7 l/min/m²) or fog to the tank surface to absorb heat and maintain a lower temperature. Caution is necessary when directing a spray onto insulated tanks so as not to destroy the insulating material. If a tank has a cooling system, verify that the cooling system is turned on and operating at maximum capacity. Closely monitor the temperature of the storage tank. If the temperature of the ester is rising despite the application of cooling water and the cooling provided by the cooling system, it may be necessary to add a shortstopping agent. If the temperature of the ester equals or exceeds 50°C, then a shortstopping agent should be added to limit the consequence of the acrylic ester polymerisation. Please note that shortstopping systems are optional and each facility must evaluate its risks associated with handling and storing acrylic esters and determine the necessity for a shortstopping system.
12. Appendix

12.1. Incompatible Materials

Almost any contamination can potentially destabilise the monomer and should be avoided. The following is a partial list of chemicals which are considered to be incompatible with acrylic esters. In most cases, these contaminants cause polymerisation of the monomer.

1. peroxide or peroxy- in name
2. per in name, e.g., t-butylperacetate
3. peresters or peroxyesters
4. percarbonates or peroxycarbonates
5. hydperoxide or hydperoxy- in name
6. azo compounds
7. azides
8. ethers
9. amines
10. conjugated polyunsaturated acids and esters
11. aldehydes and some ketones
12. reactive inorganic halides (e.g. thionyl chloride, sulfuryl chloride)
13. caustics (e.g., NaOH, KOH, Ca(OH)₂)
14. strong mineral acids (e.g., nitric, sulfuric, hydrochloric acids)
15. oxidising agents (e.g., chromic acid, permanganates, nitric acid)
16. varnish
17. inert gases (<5% vol. % oxygen)
18. carboxylic acid anhydrides
19. mercaptans (thiols)

12.2 Suggestions for an Acrylic Ester Tank

Figure 1 Components of a Storage Installation for Acrylic Esters
<table>
<thead>
<tr>
<th>Mark</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The emission control device can be an exhaust gas purification.</td>
</tr>
<tr>
<td>2</td>
<td>Heat exchanger, Temperature Control, Cooling media supply and in some cases also an insulation on the tank are required if the recommended maximum temperature of storage cannot be maintained.</td>
</tr>
<tr>
<td>3</td>
<td>The tank level should be measured by either a mechanical, a pneumatic (air aerated), or an electrical level gauge. In order to prevent overflow the tank level should be controlled by a high level gauge that can close the automatic valve.</td>
</tr>
<tr>
<td>4</td>
<td>A conservation valve protects the tank shell in case design pressure is exceeded. Various but more or less equivalent designs are commercially available.</td>
</tr>
<tr>
<td>5</td>
<td>The vapour return line minimises emissions. For fire protection the vapour return line must be equipped with at least one flame arrestor. The line has a slope so that any condensed liquid is drained back through a valve or directly into the tank. The flame arrestor should visually be inspected for free passage (polymer formation!) prior to using the line.</td>
</tr>
<tr>
<td>6</td>
<td>Drain valve and sight glass. Empty out, if condensed material from vapor return line is visible.</td>
</tr>
<tr>
<td>7</td>
<td>Product off-take to consumption (application process).</td>
</tr>
<tr>
<td>8</td>
<td>At least 2 temperature elements located −180° apart at the bottom of the tank should be present. Temperature indicator with high alarm.</td>
</tr>
<tr>
<td>9</td>
<td>Temperature indicator or control with high alarm.</td>
</tr>
<tr>
<td>10</td>
<td>Truck pad with collecting pit.</td>
</tr>
<tr>
<td>11</td>
<td>The container should be electrically interconnected with the tank and properly grounded.</td>
</tr>
<tr>
<td>12</td>
<td>Drain valves for pump and line system.</td>
</tr>
<tr>
<td>13</td>
<td>Earthing (grounding) of tank.</td>
</tr>
<tr>
<td>14</td>
<td>An automatic valve operated by the level switch allows unloading only if sufficient storage capacity is available. In order to prevent back flowing of ester in case of a pump failure the unloading line must be fitted with a check valve. The same pump is drawn to effect the unloading, recirculating and supply service. Special requirements can make it necessary to install two or more pumps.</td>
</tr>
<tr>
<td>15</td>
<td>A slight slope of the tank floor combined with a pit facilitates the complete drainage of the tank.</td>
</tr>
<tr>
<td>16</td>
<td>Diked area around tank and pumping station to collect spills.</td>
</tr>
<tr>
<td>17</td>
<td>Temperature indication with high alarm and interlock at the product pump to protect pump.</td>
</tr>
<tr>
<td>18</td>
<td>From overheating and to avoid polymerisation.</td>
</tr>
<tr>
<td>19</td>
<td>The container is connected to the system by two metal reinforced flexible hoses. Hoses should be dedicated to single service in order to exclude contaminants.</td>
</tr>
<tr>
<td>20</td>
<td>Flow indication with low alarm and interlock at discharge of product pump to protect pump from dry running and deadheading (overheating).</td>
</tr>
<tr>
<td>21</td>
<td>Conventional screw-on joints are often used. The use of a dry disconnect joint minimises the loss of ester and should therefore be considered.</td>
</tr>
<tr>
<td>22</td>
<td>An injector pipe where the outlet is below the low level switch point or a dip tube prevent excessive mist formation during unloading and recirculation operations. A location should be chosen which prevents a short circuit of recirculation. (See Chapter 7.2.11.)</td>
</tr>
<tr>
<td>23</td>
<td>In the event of a worst-case runaway all pressure outlets might be blocked by polymer. The tank shell can best be protected from rupture by a weak seam roof.</td>
</tr>
<tr>
<td>24</td>
<td>For the control of the monomer temperature in hot climates, excessive absorption of heat from sun irradiation can be prevented by painting the tank with a heat reflecting, white coating.</td>
</tr>
<tr>
<td>25, 26</td>
<td>Possible connection for restabilisation (shortstop) system.</td>
</tr>
</tbody>
</table>
12.3. Suggestions for an Exhaust Gas Purification

Figure 2  Example of a Scrubber for the Purification of Acrylic Ester Loaded Exhaust Gas

1. The inlet valve can be designed for manual operation or as a flow control valve. If water is used as an absorbent a continuous flow should be maintained. The overflow is disposed of into a sewer routed to a biological wastewater treatment. If this is not available diluted sodium hydroxide should be used as absorbent.

2. Suitable material for the container and the column is stainless steel or glass fibers reinforced resin.

3. For the random packing, Raschig rings or any other packing material may be used. The insert of 2 distributor trays is recommendable. The packing may be stainless steel or plastic material. For stability reasons trays should be made from stainless steel.

4. Recirculation pump according to design data.

5. Flow restriction for the absorbent in the bypass. If too much absorbent is fed into the column the free gas flow is suppressed and pressure will build up. With insufficient feed of fluid the washing efficiency is unsatisfactory.

6. A conical nozzle uniformly distributes the absorbent on the packing. If packing of the column is not uniform the gas escapes through a coherent channel and no washing is achieved.

7. Overflow into the sewer (only if routed into treatment plant).

8. Valve for complete drainage of the container.

9. Outlet for the purified exhaust gas.
The following layout data are suggested:

<table>
<thead>
<tr>
<th><strong>Volume [m$^3$/h] of absorbent in recirculation:</strong></th>
<th>2 to 4 % of gas volume V in [m$^3$/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diameter D [mm] of column:</strong></td>
<td>15 to 25 times the square root of the gas volume V in [m$^3$/h], corresponding to a gas velocity of approximately 0.5 to 1.5 [m/sec].</td>
</tr>
<tr>
<td><strong>Length L [mm] of column:</strong></td>
<td>Approximately 10 to 20 times the diameter D [mm]</td>
</tr>
</tbody>
</table>