

Scope: "Glacial Acrylic Acid (GAA)

Heating stations for tank trucks and tank containers in Europe

Monomers

- Monomers are chemicals that can react with themselves to form chains, called polymers
- Monomers are useful because of their ability to polymerize
- This same quality that makes them useful, also make them dangerous when stored or handled improperly

Polymerization is exothermic: an unexplained temperature increase could indicate an unstable or reacting material.

ATTENTION: A temperature increase beyond 30 °C may be dangerous and corrective actions have immediately to be taken during a heating process.

Overheating becomes especially critical if inhibitor and dissolved oxygen are not present at saturation levels in the product. Therefore the recommendation is to limit the heating medium temperature to 35°C whilst a range of up to 45°C may be safe if proper inhibitor levels are maintained by thoroughly mixing the product or by other means (please refer to [Inhibitor Depletion, page 9](#) and [Inhibitor Deactivation/Oxygen Depletion, page 9](#)).

Attention

Product temperatures of 30°C and higher can be hazardous and must be avoided during warming/heating and especially during thawing operations. The temperature of the heating medium must not exceed 35°C for safety reasons.

Safe thawing of acrylic monomers

UNDER NO CIRCUMSTANCES SHOULD LIVE STEAM BE USED TO HEAT OR THAW ACRYLIC MONOMERS

Acrylic acid has high freezing point:

- Acrylic acid 13 °C

Frozen monomer presents a risk due to the dangers of unsafe thawing. Freezing is a purification process and inhibitor preferentially partitions into liquid, leaving purified frozen monomer. Thawing frozen, uninhibited monomer is hazardous.

Bulk containers containing frozen monomer can be safely thawed through by circulation of tempered water through the heating coils. The temperature of the water should never exceed:

- max 35 °C

Use only automatic temperature controlled, “Fail Safe” alarmed, tempered water systems. The temperature of both the circulating water and the thawed portion of the monomer should be closely monitored. If possible, the monomer should be well mixed to ensure that dissolved oxygen and the inhibitor is well distributed during thawing as well as to enhance heat transfer.

Never use the direct application of live steam in tracing or coils to heat or thaw acrylic monomers. There is no practical way to limit and control the temperature of steam below the maximum allowed temperature of 35°C for the heating medium.

Never withdraw material from a partially frozen or partially thawed container of acrylic acid. Such material may have low inhibitor levels or it may contain most of the inhibitor required for the entire contents of the container.

If possible, contents should be thoroughly mixed during and after the thaw cycle to ensure uniform mixing of the inhibitor before any liquid is withdrawn. If possible, mix by re-circulation, agitation, or by means of an eductor.

If frozen monomer is discovered in a vessel after emptying, return warm monomer to the vessel to provide inhibitor and a heat transfer source for thawing.



SUMMARY

- NEVER USE STEAM as the heat transfer fluid or heating medium
 - Localized hot spots must be avoided
 - Never apply steam to the outside of the container
 - Never connect heating mantle to steam or apply live steam to surface!
 - Never store adjacent to heat sources.
 - Never apply electric heating bands to thaw containers as these generate high surface temperatures.
 - Never use steam-water mixing nozzles or tees directly in heating coils, jackets, etc., for thawing. An increase in steam pressure or loss of water supply would create immediate high temperature conditions resulting in a polymerization.
 - Electrical heating blankets temperature controlled and with limited power consumption may be used as well.
 - Since only low temperature heating must be applied to acrylic acid, venting of the tank container to the outside is not required during the heating process. Nevertheless if the heating station has the technical facilities to connect to a vapor exhaust line, it can be used for additional safety.
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Temperature measurement requirements

In case heating stations are used to keep a loaded truck in the temperature specifications range, a good safety system must be available at the heating station site.

- At least one Temperature sensor either being introduced via the vapor return line into the Acrylic Acid clearly reaching into the liquid (e.g. 70% filling degree of the tank). An alternative is a dip tube sensor that comes along with the tank container.
- Multiple (>2) control barriers (temperature alarms and interlocks) to avoid too high water temperature and product temperature (*as specified in the specification: between 15 – 25 °C*).
 - Feed water (or other heat transfer liquid) temperature hardware interlock on feed pump and feed valve (2 actors either pump and valve or 2 valves, valves are to be designed normally closed)



- Feed water temperature indication and alarm
- Product temperature indication and alarm
- 24/7 manned control room
- Use of data system for temperature settings and alarms

The design of heating devices must include control instruments that are suitable to reliably prevent overheating the acid. One such system is a double-circuit warm water system with steam or hot water in the primary and a glycol-water mix in the secondary circuit. A heat exchanger is commonly used to achieve the transfer between the circuits. Provision must be made to automatically control and alarm the temperature in the secondary circuit at preset high and low points. Maximum permissible temperature in the secondary circuit is 35 °C inlet temperature at the tank container minimum temperature should be set at 18 °C. Under no circumstances should live steam come in contact with acrylic monomer. The primary circuit must shut off automatically if instruments fail and the preset high temperature is reached.

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Shortstop inhibitor: PTZ

Monomers are self-reactive due to free radical polymerization. Sources of free radicals can be natural-occurring (thermally generated, peroxide formation), due to contamination, or deliberate (e.g., peroxides/persulfates used in polymer manufacturing). Polymerization is exothermic: an unexplained temperature increase could indicate an unstable or reacting material.

- Short-stopping is a term used for the emergency re-stabilization of an unscheduled acrylic monomer polymerization event.
- If you become aware of an acrylic monomer polymerization event (unexplained increase in temperature and/or pressure, vapor venting, etc.) please contact emergency services immediately for guidance.

PTZ in solution is the preferred shortstop agent for acrylic monomer. 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 monomers with gross amounts of polymerization initiator or a delay in activation of the shortstop system. Enough shortstop inhibitor needs to be available to reach the target concentration in the monomer.

The final concentration of PTZ in the acrylic monomer to be shortstopped is suggested to be in the range of 200 to 1000 ppm. However, in the case of contamination, restabilization may not be possible at any concentration of PTZ, depending on the nature and concentration of the contaminant.

Commercial PTZ solutions are available (Restab, Allesan, LVT...) please contact your supplier/emergency contacts.

Preparedness: If you handle acrylic monomers, you should have access to a supply of PTZ as appropriate for the volume of material handled.

ATTENTION: Do not approach a tank whose contents have reached or exceeded 60 °C



Temperature ranges

Early detection of a high temperature inside an acrylic acid vessel can facilitate timely emergency response to a dangerous inadvertent polymerization and may help avoid serious injury and/or loss of property.

<u>Product</u>	<u>min Temp C</u>	<u>max Temp C</u>
GAA	15 °C	<= 25 °C

Emergency Services must be called

- If product temperatures are outside of the maximum temperature range
- At unexpected temperature rise of > 5 °C /hour

Emergency contacts

- Arkema France +33 3 87 93 8500
- BASF SE +49 180 2273 112
- Dow Europe GmbH +31 11 5694982
USA 24-Hour Emergency Contact: CHEMTREC +1 800-424-9300
- Evonik Superabsorber GmbH +49 2365 49 22 32
- Synthomer a.s. +420 352 614222

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