

Emergency Restabilisation with RESTAB™ Technology



 **BASF**
We create chemistry

MEET THE EXPERTS IN SAFE HANDLING OF ACRYLIC MONOMERS.

BASF has a long history of producing and using acrylic monomers and has been handling acrylic monomers on an industrial scale since 1936. The amazing properties of various polymers produced from acrylic monomers and their comonomers can be attributed to the high reactivity of acrylic monomers. This high reactivity has to be tamed till you want it to unfold its properties. Storage inhibitors are used to provide this taming effect. Usually dissolved oxygen and MeHQ are used for this purpose. Contrary to other inhibitors they can easily be switched off, if desired.



What are possible safety issues with acrylic monomers?

The ease of use of the storage inhibitors bears the risk, that accidentally the storage inhibitors may be switched off. This can be caused by contamination, oxygen depletion or excessive heat. This will eventually unfold the high reactivity of the acrylic monomer at a location where it is not intended to do so, where there are no technical means to handle that kind of reactivity. Uncontrolled polymerization is rapid and can be very violent, generating large amounts of heat which increases the pressure. This increase in pressure causes the ejection of hot vapor and polymer which may autoignite.

What's at risk?

Runaway polymerization reactions of acrylic acid can cause injuries, damage to production facilities, and even loss of life. Accidents like the ones in southern Germany in 1994 and Japan in 2012 have clearly shown this.

How RESTAB™ brings restabilization.

BASF has developed RESTAB™, a technology package that restabilizes acrylic monomers by catching a radical chain polymerization at an early stage. RESTAB™ provides stability in situations that may otherwise get out of control.

// Re-Stabilizing reactivity with RESTAB™

restabilizes acrylic monomers by catching a radical chain polymerization at an early stage, providing stability in situations that may otherwise get out of control.

RESTAB™ units are basic, essential safety equipment, just like fire extinguishers





WHY THERE ARE FOUR GOOD REASONS FOR RESTAB™.

// 1. SAFETY:

- RESTAB™ can be applied from a remote safe haven (e.g. sheltered location).
- It is a self-contained system that does not require electric energy or other energy sources to be available in case of emergency.
- Dry disconnect couplings reduce the likelihood of an accidental spill to a minimum.

// 2. RELIABILITY:

- Components used are robust and widely used in safety equipment.
- Design is limited to the minimum amount of components in order to reduce the likelihood of a component failure.
- Thorough testing of the entire system and individual components was performed prior to technical implementation.

// 3. SPEED:

- Strong similarity to fire extinguishers therefore easy to use for emergency responders.
- Quick connect system implemented.
- Optimized high concentration of stabilizer for low dosage time.
- Fast gas induced mixing technology included.

// 4. SCALABILITY:

- Products or vessels requiring a higher concentration of emergency stabilizer can be restabilized with multiple units (serial connection of multiple units).
- Large storage tanks do not require an individual design of the system but can be equipped with a manifold (parallel connection of multiple units) to cope with mixing requirements.
- For very large storage tanks 500 liter units using the same design principle are available.

MOBILE RESTAB™ UNITS

// MAY BRING CONSIDERABLE COST SAVINGS
COMPARED WITH DEDICATED SYSTEMS.



RESTAB™ Container types	Gas type	In general suitable for tank sizes in between of
RS 50/2	Lean Air	50–1,000 m ³
	94% nitrogen 6% oxygen mixture	Stabilizing storage tanks larger than 100 m ³ may require application of multiple containers



RESTAB™ Container types	Gas type	In general suitable for tank sizes in between of
RS 500	Lean Air	500–5,000 m ³
	94% nitrogen 6% oxygen mixture	Stabilizing storage tanks larger than 500 m ³ may require application of multiple units

//1.

Why safety always comes first.

Safety features are a key part of the design and operation of storage and handling facilities. The fundamental elements of safety design are temperature control, redundant temperature monitoring and alarms that cannot be ignored, effective recirculation and mixing, oxygen-containing blanket gas (5 to 21 vol. %), dedicated piping and equipment to prevent contamination. A properly designed facility must also use appropriate safety procedures. But even in a facility that is properly designed and run, there is no guarantee that accidents won't happen. That is why BASF recommends additional protection using RESTAB™.

A well designed RESTAB™ system can be applied from outside the banded area of the tank farm. Feed pipelines may be designed up to a length of 100 m. This allows the emergency responders to be at a distance from the storage tank and potentially have a sheltered location while injecting the RESTAB™ into the storage tank.

In case of an accident involving a fire electric energy or other energy sources may not be available any more. Therefore RESTAB™ was designed such that it does not require external energy. The only source of energy required comes with the system and consists of pressurized oxygen-containing gas, that propels the phenothiazine (PTZ) inhibitor solution into the storage tank and after having done so provides a gas flow that allows for gas induced mixing of the tanks contents.

//2.

How reliability makes safety even safer.

RESTAB™ system components are widely used in fire extinguishers and have a long standing history of reliability. The design of the system has been limited to the minimum amount of components in order to reduce the likelihood of a failure of the entire system.

In addition, the entire system has undergone thorough testing with the PTZ solution prior to technical implementation. RESTAB™ can be purchased from BASF licensees. We only license RESTAB™ technology to manufactureres of safety equipment with a long-standing reputation in this area.

RESTAB™ systems have been sold and used for over a decade, and maintenance records indicate only minor room for improvement. In several known cases of emergency, the system has proven to work reliably.

//3.

How speed contributes to safety.

Speed is the key factor of success in emergency response. Successful restabilization requires a timely response to the detection of a significant temperature increase. It is therefore crucial that facilities implement the temperature alarms and required actions indicated in the table on page 10.

Emergency responders will have no difficulties handling the RESTAB™ system since it is very similar to fire extinguishers. The quick connectors provide an additional safety margin through speed of connection and a leakage free coupling.

A proper design of the feed pipe to the storage tank allows for dosage times in the range of 1-5 minutes for a single unit. In addition, the gas induced mixing option of the RESTAB™ will, if properly applied to the tank installation, allow a complete mixing of the PTZ inhibitor with the tanks contents in less than 20 minutes.



//4.

How the scalability of the RESTAB™ system is achieved.

Because a high loading solution of PTZ in the solvent can be achieved, the emergency solution container can be kept small and mobile. The advantage of non-dedicated, mobile RESTAB™ units is obvious: no dedicated canisters to individual tanks are needed and storage facilities with multiple tanks require only a limited number of RESTAB™ units. The cost savings may be considerable compared with dedicated systems.



For larger storage tanks parallel injection via a manifold may be necessary to provide sufficient PTZ and/or sufficient gas flow for mixing of the tank.

Manifold types used to connect several RESTAB™ units in parallel

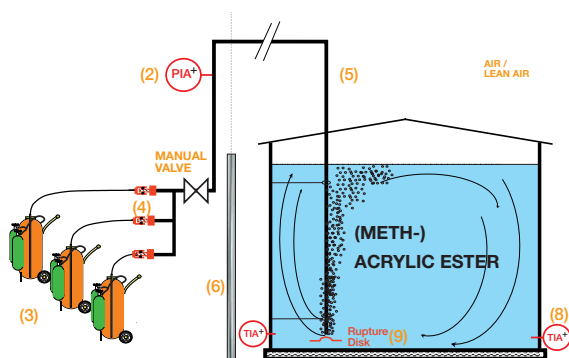
How to connect RESTAB™ to the storage tank.

The following diagrams represent two possibilities for injecting the stabilizing solution into a storage tank. Both systems can be optimized to ensure the mixing of the liquid solution of PTZ even in the event of a

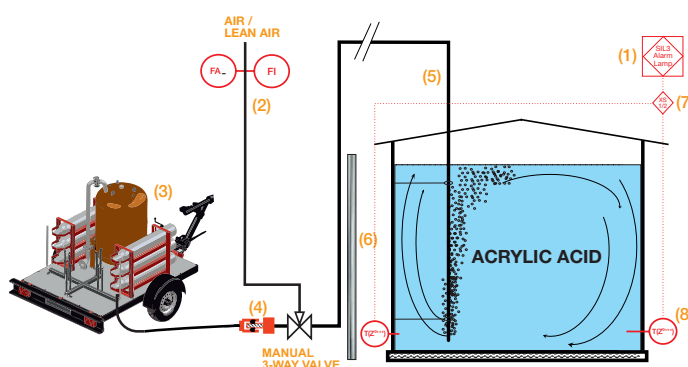
power failure. Still, it is advisable for facilities to have backup systems for electricity, compressed air and other power sources.

Injection system schematics for various tank installations

System 1)



System 2)



KEY TO THE DIAGRAMS:

- (1) A "SIL 3 level alarm lamp" that cannot simply be muted by a push button. The signal needs to be visible for all operating personnel as long as the alarm condition is in place. The control room has to be manned 24/7.
- (2) This alarm (pressure or flow) is an indication whether the protection to keep the pipeline free of polymer is intact. Either the rupture disc or the air flow keeps the monomer out of the pipeline.
- (3) Mobile RESTAB™-Units can be used in parallel and in sequence depending on tank size and restabilization requirements. Mobile units may be used for different tanks. The feed pipeline and its connection manifold have to be dedicated to the individual tank.
- (4) The mobile unit is connected via a dry disconnect coupling. Only after the valves at the RESTAB™-Unit have been opened is the manual valve opened.
- (5) In all setups, the RESTAB™ solution must be fed directly into the storage tank via a dedicated pipeline. The pipeline design allows the pressurized gas to convey the restabilization liquid completely through the vertical sections of the pipeline.
- (6) A fireproof wall either directly next to the banded area or at a distance. This allows the mobile unit to be connected safely even when there is a fire inside the banded area of the storage tanks.
- (7) Alarms should be initiated by a 1 out of 2 selection (1oo2). If the tank contains a higher number of temperature probes, we suggest a 1 out of n (1ooN) alarm trigger.
- (8) The temperature probes should be independent, as far from each other as possible, and always covered by liquid. The thermocouples installed should be SIL 3 quality for glacial acrylic acid storage facilities and enhanced DCS quality for storage of the other acrylate and methacrylate monomers. The temperature probes should consist of redundant components.
- (9) A zero void volume rupture disk at the end of a dip tube, to keep the RESTAB™ pipeline clear. System design should allow technicians to take out the dip tube and repair the rupture disk without having to empty the tank. Alternatively, the pipeline can be kept clear using a constant flow of air. In this case, a low flow alarm should be used instead of a low pressure alarm.

WHEN TO TAKE ACTION WITH THE RESTAB™ SYSTEM.

First Choice for Secondary Defense.

The RESTAB™ system is designed as a secondary defense for situations where primary safety control devices have failed or where unforeseen circumstances have created a critical situation. It should never be a substitute for good preventive safety programs. Restabilization with PTZ inhibitor is considered the very best emergency response for an uncontrolled polymerization, such as might be caused by accidental overheating or accidental depletion of dissolved oxygen/stabilizer might be caused by robust pool fires. Early detection of unsafe conditions inside or around the tank is a key task for a timely restabilization.

All tanks must be equipped with redundant temperature probes, temperature indication, recording and several alarm levels have to be implemented.

Recommendations for such set points are given in the following table. Storage temperatures greater than the industry-recommended target values T1 or an unexplained temperature increase, even at temperatures below T1, are indications that dangerous conditions may be developing.



Monomer	T0 °C	T1 °C	T2 °C	T3 °C	T4 °C
Glacial Acrylic acid	15	25	30	35	60
Glacial Methacrylic acid	18	35		40	
Acrylate or Methacrylate esters	In most cases not applicable	35	35	40	60

T0 Represents the lowest storage temperature, which is set at least 2 °C above the freezing point of the monomer. Freezing should be avoided at all costs because the stabilizer does not crystallize, producing a crystallized phase that does not contain stabilizer. This temperature is only important for acrylic and methacrylic acid, as all the other acrylates have a very low freezing point (< -60 °C).

T1 Recommended maximum storage temperature. Temperatures above this should be avoided to prevent a premature consumption of the inhibitor system. Provided the temperature of the material has not exceeded T1 and the concentration of inhibitor is correctly maintained, safe storage of 1 year can be expected.

T2 Temperatures of T2 or higher can be hazardous and must be strictly avoided. The temperature alarm should be activated once T2 is reached to allow sufficient time for investigation and potential emergency response. Operating procedures must clearly request corrective actions (e. g.: verify temperature, bring down temperature by cooling or blending, check inhibitor concentration).

T3 Temperatures of T3 require immediate emergency response. RESTAB™ must be activated before temperatures of 45 °C are reached. Several emergency response drills at BASF have shown that it takes 30 minutes to get the short stopping system in place, have every instruction followed and the system ready to be launched. Hence, the temperature, when emergency response has to be called, is less than 45 °C. Please check your response times in a drill thoroughly if you are not sure whether 30 minutes can be met or if you want to set a higher alarm threshold.

T4 If this temperature is achieved during storage, the evacuation procedure must be initiated. It is assumed that the emergency response team is already on the spot because they should have been called before initiating the RESTAB™ system and are preparing the evacuation should the temperature continue to rise.



WHY CHOOSE A RESTAB™ SYSTEM.

While BASF recognizes that emergency restabilization is never a substitute for good preventive safety programs, the use of RESTAB™ will minimize the impact of an unscheduled polymerization. Even a well-designed tank storage system cannot guarantee that no accidents will happen. This is why precautionary measures are so important. Fire extinguishers, LEL detectors and foam injection systems save lives and protect the environment.

The RESTAB™ system, too, is an essential precaution. Since the potential damage of runaway polymerization reactions is considerable, facilities handling acrylic monomers should install the RESTAB™ system to increase response capability. RESTAB™ helps you re-establish safety in dangerous situations.

If you are interested in buying RESTAB™ UNITS, please contact our licenced RESTAB™ UNITS manufacturers RS Roman Seliger or TOTAL Feuerschutz.



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