

Max-Amine* 70B

Controls Amine System Foaming

Key Points:

- Max-Amine 70B is uniquely formulated to reduce foaming in amine systems using MEA, DEA, MDEA, DGA and formulated amine solvents.
- The research and technology division for a major oil refiner has approved Max-Amine 70B for use in amine systems including those upstream to alkylation and other sensitive process units.
- Max-Amine 70B has been proven to be more cost effective than silicone, polyglycol or alcohol based products.
- In contrast to silicone based defoamers, Max-Amine 70B does not increase equipment fouling, particulate filtration costs and the emulsification tendency of the amine.
- In contrast to many polyglycol based defoamers, Max-Amine 70B does not degrade to fatty acid soaps that increase foaming.
- In contrast to alcohol based defoamers, Max-Amine 70B does not degrade to organic acids.

Superior foam control combined with negligible side effects make Max-Amine 70B an excellent product to use for controlling foaming problems in amine systems.

Applications

Max-Amine 70B is a defoamer (or antifoam) formulated for use in amine systems that remove carbon dioxide (CO₂) and hydrogen sulphide (H₂S) in gas processing applications such as:

- Natural gas processing
- Refinery amine systems
- Hydrogen production
- Ammonia manufacture

- Coke oven gas processing
- Cryogenic gas processing and
- Synthesis gas purification.

Max-Amine 70B is newest generation defoamer of GE Water & Process Technologies for use in amine treating gas and liquid hydrocarbons. Max-Amine 70B should be considered as an alternative to upgrading equipment to control hydrocarbon entrainment, amine losses or for incremental increases in unit throughput.

Max-Amine 70B has proven to be effective in field and laboratory tests in MEA, DEA, MDEA, DGA and formulated amine solvents.

Experience In Europe

The following write up has been taken from an internal newsletter distributed worldwide by the research and technology division for this refining company. Changes were made only to remove the name of the operating company, refinery location and the addition of American units. This application resulted in an immediate savings of US\$250,000 for a chemical cost of only US\$6,500, a return of over 4,000%.

"In April 1998, a refinery in the United Kingdom switched to a novel antifoaming agent, a product called Max-Amine 70B, supplied by GE. The switch followed a period of extreme foaming, which caused their amine system to have serious operational difficulties. The result has been dramatic with the complete elimination of operational upsets due to foaming and flooding.

This refinery amine system has an inventory of 200 tons (441,000 lbs) of 40 wt% DIPA, circulates



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440 gpm (100 m³/h) of solvent to 3 treaters: a dry gas absorber and LPG treater on the cat cracker gas plant and a propane treater on one of their crude distiller units.

Following a major turnaround in February 1998, severe problems with foaming and flooding of both the amine regenerator column and dry gas absorber were encountered. Part of the problem was traced to problems with the regenerator column internals, which had been replaced at the shutdown. These were subsequently rectified. It was recognized though that, for reasons still not fully understood, the foaming tendency of the amine solvent was intrinsically high.

Like most other amine units, this refinery had been using a silicone-based antifoam to alleviate the problems of foaming; relying on the intervention of operators to stabilise the system during foaming events by shot dosing of antifoam. Such antifoams, however, have always had two drawbacks:

1. They cannot be dosed in a manner which will prevent foaming so rely on careful operator attention to act in time,
2. If overdosed they can start to contribute to foaming.

It was almost by chance that the refinery learned of a novel antifoaming agent, Max-Amine 70B, a high molecular weight polyalkyl oxalate, marketed by GE. This product is fundamentally different from silicone-based antifoams in that it is designed to be added continuously to reduce the intrinsic foaming tendency of the solvent and hence eliminate foaming. GE could only provide one reference for this product in Europe, but the experience of this refinery was very positive.

On the basis of this reference, the refinery started a trial with Max-Amine 70B and has now been using the antifoam since April 1998. Without Max-Amine 70B addition, the amine produces a foam, which typically takes 30 to 40 seconds to break following vigorous shaking in bottle. With Max-Amine 70B added at a daily rate of 10 ppm (mg/L) based on solvent volume, foam stability is reduced to between three and four seconds. This has both eliminated foaming and enabled higher stripping steam rates to be used in the regenerator.

In line with GE advice, the antifoam is injected into the rich amine return to regenerator column. At first, dosing was done on an intermittent basis with

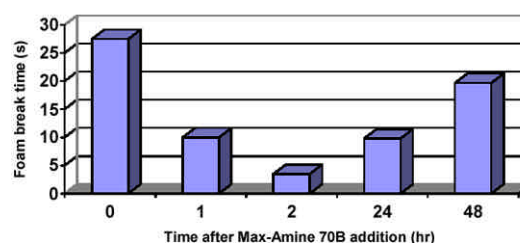


Figure 1

shot feeding 6 kg (1.6 gal) every 48 hours. This served to show that the antifoam was effective for between 36 and 48 hours. (Figure 1). The loss of effectiveness is at least in part attributed to absorption onto the activated carbon filter in the system but GE also claims that the product slowly breaks down to alcohols which are removed by the bleed from the regenerator column reflux.

A move was made to continuous dosing, first at 3 kg/day (0.8 gal) and now at 2 kg/day (0.5 gal). The results have been very positive, reducing the variance in daily dP from over 200 mbar (3 psi) to less than 25 mbar (0.36 psi).

The main concern at the refinery with Max-Amine 70B was that since it has a high molecular weight molecule containing nearly 30% by weight oxygen, it could partition into the LPG stream in the LPG treater and give problems with the HF alkylation unit and Butamer units downstream. An analytical method was therefore developed for Max-Amine 70B and tests were conducted on HF alkylation unit feed. These tests showed that the Max-Amine does not extract to any significant extent into LPG.

Apart from the improved stability, the only other noticeable impact of Max-Amine 70B has been an increase in pressure drop, about 15 mbar (0.2 psi), in the dry gas absorber, which in itself has not created a problem. The refinery continues to evaluate the performance of the antifoam and are now reviewing whether Max-Amine eliminates the need for activated carbon filtration.

The conclusion – for amine systems which suffer from foaming problems which do not respond well to silicone-based antifoam – Max-Amine 70B would seem well worth a try.

Foaming in Amine Solutions

Foaming occurs as the result of the physical inclusion of gas bubbles enveloped by the amine solution. Clean amine solutions have a low tendency to foam because they are very polar and have high surface tensions. Clean amine solutions also produce foams with little stability because they have low viscosity. Foaming problems in amine units are due to contamination by materials that reduce surface tension and increase viscosity.

Low surface tension is usually associated with a high foaming tendency. This is because a low surface tension liquid allows the surface of a bubble to expand easily. Liquid from the bulk solution readily flows to the surface, allowing the bubble to form. Amine solutions, like most polar liquids, have a high surface tension as compared to hydrocarbons which are essentially non-polar. Thus, hydrocarbons are the most likely cause for an increase in the tendency of an amine solution to foam.

An amine solution that readily foams is not a problem unless the foam is stable. Increasing the viscosity of the amine solution results in slower drainage of the liquid from the bubble surface. The longer it takes for the liquid to drain from the bubble, the longer the bubble will last. Three types of compounds common in amine systems – hydrocarbons, acids and solids – will increase foaming tendency.

1. Hydrocarbons that are dissolved in the amine solution can increase the solution viscosity and slow drainage from the surface film. The impact of hydrocarbons on foaming in amine solutions is different for each amine solvent because of the difference in hydrocarbon solubility. MEA and DEA solutions have the lowest hydrocarbon solubility and are little effected by clean hydrocarbons. MDEA, on the other hand, has a much greater affinity for hydrocarbons and foam stability is greatly increased by the presence of liquid hydrocarbon.
2. Acids, particularly organic acids, greatly increase foam stability. First, organic acids can increase the solubility of hydrocarbons in the amine solution. Organic acids can also stabilize a hydrocarbon/amine solution emulsion that will slow bubble drainage. Organic acids also increase the viscosity of the amine solution and promote the formation of a gel like bubble surface film. Thus increasing acid content in the

amine solution increases the foaming tendency and stability of the solution.

3. Solids, particularly those less than 5 micron, concentrate on the liquid surface and increase surface viscosity and slow drainage. Particles that have anionic or cationic bonding sites, such as iron based corrosion products or activated carbon particles, will have a greater effect on slowing bubble drainage in polar solutions.

While hydrocarbons, acids and solids are easily identified materials that increase foaming in amine solutions, any chemical species that lowers the surface tension of the liquid film increases foaming tendency while any species that inhibits liquid drainage or increases viscosity increases foam stability.

Antifoam - Defoamer

Antifoams or defoamers are chemicals which are formulated to increase the elasticity of the liquid film on the bubble. By allowing the liquid film to expand, thin spots form allowing the bubble to rupture. Foam made from such an elastic film will be unstable. For any material to be an effective defoamer, it must have extremely low solubility in the amine solution. If it is soluble, it will not concentrate at the surface film and it would be able to migrate to the film as the bubble expands – repairing the thin spots.

Max-Amine 70B

Max-Amine 70B is a defoamer designed by GE to out perform silicone, polyglycol or alcohol based products and avoid the side effects common to these materials. Max-Amine 70B is a non-ionic polymer made of repeated polyoxyethylene and polyoxypropylene chemical groups. It is resistant to degradation and forms shorter chain length polymers upon degradation. Max-Amine 70B is removed to some extent by activated carbon filtration but is also removed in the flash drum (3-phase separator).

Testing conducted in GE's Research Laboratories reveal that Max-Amine 70B out performs silicone, polyglycol and alcohol based products in foam tests conducted using both laboratory amine solutions and actual plant amine solutions. Figure 2 and Table 1 illustrates the performance advantage of Max-Amine 70B in two refinery amine samples.

Similar testing conducted by a major amine manufacturer support the results of this testing.

While Max-Amine 70B outperforms other defoamer and antifoam products, the most important benefit of this product is the absence of the following side effects:

1. Max-Amine 70B does not increase equipment fouling, particulate filtration costs or the emulsion tendency of the amine solution, in contrast to silicone based products.
2. Max-Amine 70B does not breakdown to fatty acids or fatty acid soaps that increase foaming, in contrast to polyglycol ester based products.
3. Max-Amine 70B does not breakdown to form organic acids, in contrast to alcohol based products.

As of November 1998, 29 amine systems located in the United States and Europe were using Max-Amine 70B. Of these, 23 are refinery amine units, 2 are coke oven gas plants and 4 are natural gas processing plants. Additional systems in Canada, South America, Africa and Asia are using Max-Amine 70B.

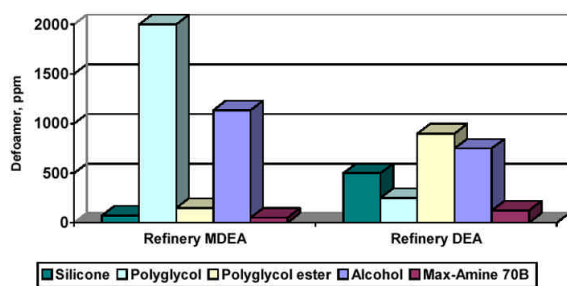


Figure 2: Defoamer performance in refinery amine samples (treatment required to completely suppress foam)

Table 1: Defoamer Performance and Sludging Potential

Defoamer	Refinery MDEA 140F (ppm)	Refinery 75F (ppm) DEA	Surface Appearance (after 12 hours)
silicone	74	500	floating flocs
polyglycol	>2000	250	clear liquid
polyglycol ester	150	900	no surface layer
alcohol	1135	750	clear liquid
Max-Amine 70B	51	125	clear liquid

nitrogen flow at 800 ml/min, size D frit.

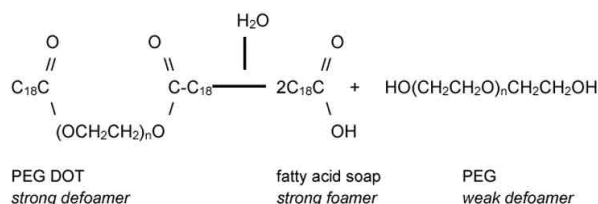
ppm based on actives required to completely suppress foam

Silicone Antifoams

Silicone based defoamers are composed of a silicone compound (such as dimethyl polysiloxane) emulsified in water or hydrocarbon oil. (methyl acrylic acid is most often used to form the dispersion). Silicone based products are used for foam control in a wide range of process systems including cokers, sour water strippers and amine systems. Most of these systems are "once-through" and no serious side effects will be noted. Amine systems are not once-through and defoamers tend to remain in the system for several days. Silicone based products, in particular, tend to coat metal surfaces, filter media, and particles in the system. These products also increase the emulsification tendency of the amine. These side effects lead to equipment fouling, increased filtration costs and higher amine losses.

Polyglycol Antifoams

Polyglycol based defoamers include a large number of compounds based on polyethylene glycol (PEG) and polypropylene glycol (PPG). These defoamers may also contain co-solvents to produce a uniform product. A polyglycol ester is the reaction product of a polyglycol and a fatty acid. Polyglycol esters (such as PEG DOT) are often much better defoaming agents than the non-ester polyglycol. Unfortunately, the ester readily hydrolyses back to the polyglycol and fatty acid. The fatty acid soapifies – it forms a soap with very strong foaming properties. The formation of soaponified fatty acids in once-through systems (such as a sour water stripper) is of little importance but in a closed system, like an amine unit, it creates a cycle of increasing foaming severity.



Alcohol Defoamers

Alcohol based defoamers are made of unsaturated fatty alcohols with about 16 to 20 carbon atoms. Oleyl alcohol is a common example. Like silicone and polyglycol based products, co-solvents may be included to produce a uniform product. As compared to silicone based products, alcohol defoamers are generally less effective but less expensive. The problem with alcohol based defoamers is their rapid degradation to organic acids. Formic and acetic acids are common degradation products but longer chain acids are also formed. The longer chain length acids can result in more serious foaming problems.

Max-Amine 70B Application

The most common location for foaming in an amine system is in gas treaters or absorbers. Foaming in amine absorbers can result in reduced treating capacity, off specification products and high amine losses. If the problem is condensing hydrocarbons, the foaming may be resolved by increasing the Lean Amine temperature. If hydrocarbons are entrained in the gas feed, increasing the temperature may have little or no effect.

The injection of Max-Amine 70B into the Lean Amine feed to the absorber(s) should resolve the foaming. It can be injected with "shot feed" injection equipment or with a chemical injection pump. For shot feed applications, two to four quarts are injected at a time. The dosage for a continuous injection system is typically 10 to 50 ppm (mg/L)/day based on system volume.

The use of Max-Amine 70B has also been beneficial in improving the separation of gas, liquid hydrocarbon and amine solution when injected into the Rich Amine upstream to the Flash Drum.

One of the most serious locations for foaming is in the regenerator. Foaming in the regenerator usually corresponds with a loss of liquid level in the bottom of the tower, reduced tower top temperature and a higher Lean Amine loading. Reducing the steam rate may allow the hydrocarbon to descend in the tower, reducing the foaming by reducing vapor traffic. Alternately, a small amount of Max-Amine 70B injected into the Rich Amine or Reflux can help

resolve the problem. Hydrocarbons that vaporize overhead should be removed by purging the reflux accumulator to the waste water system.

As with any foaming control chemical, the presence of other antifoams may have a negative side effect on performance. Whenever possible, allow several hours or even days for one antifoam product to exit the system prior to injecting a new product. Max-Amine 70B has been found to be compatible with most polyglycol and alcohol type of antifoams but high concentrations of silicone based products reduce its performance.

Determination of Foaming Tendency and Stability

This is a simple procedure that can be used to determine the foaming tendency and stability of an amine solution. If the defoamer products are to be evaluated, the amine solution should be allowed to settle in a separatory funnel for at least one hour before the bottom layer is used for the evaluation. The amine solution should be heated to 100°F (37.8°C) or the Lean Amine feed temperature to the absorber.

Equipment

1 liter graduated cylinder gas flow meter (500 to 5000 ml/min) gas supply – nitrogen or air timing device connecting tubing hot water bath sparger tube – sintered glass, metal or ceramic.

Procedure

1. Pour 200 ml of 100°F (37.8°C) amine solution into the graduated cylinder.
2. Establish gas flow at 4,000 ml/min. Insert sparger tube and begin timing.
3. Record foam height after one minute. Stop gas flow and reset timer.
4. Record time required for foam to break to a liquid surface.
5. Thoroughly clean cylinder and sparger tube before and after each use.
6. Repeat, adding defoamer product at desired concentration.

Note: If foam exceeds height of cylinder, repeat using a lower gas rate.