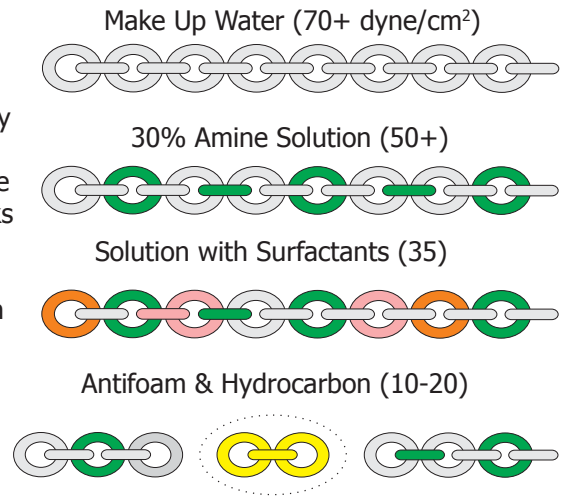
D-Foam INCORPORATED
Foaming Abatement

The SigmaPure System

Simultaneous Treating and Troubleshooting Amine Plant Foaming

Amine plant foaming is a common, but misunderstood phenomenon. It is safe to say that every amine plant in the world will eventually experience solution foaming. Given similar solution strengths, foaming in these systems is caused by solvent chemical contamination, over frothing due to tower internal mechanical damage, or a combination of both. As tower internals become restricted they either begin to flood because of liquid hold up or produce more froth due to gas jetting. Froth resists breakage (disengagement) as it becomes contaminated with surfactants and produces foam.

One of the most misinterpreted solution properties used as an indicator of foaming potential is surface tension. Surface tension is a measure of the interactive nature between interface molecules. Low surface tension liquids are mistakenly assumed to have high foaming tendencies. For example, low surface tension soaps will not promote foam unless their interfaces are strengthened by adding water. A good gas - liquid interface analogy would be a length of chain with interactions between surface molecules as links. Water has strong molecular interaction, strong links; therefore high surface tension. Every liquid, including multi-component solutions and mixtures, has a surface tension based on the strength of its chain links. The molecules of surface active agents (surfactants) are weak links in the interfacial chain. Greater the surface activity creates weaker links. The surface tension of a clean solution will generally be higher than the same solution contaminated with surfactants. Since amine solvents are solutions containing several liquid fractions their surface tensions vary somewhat with the concentration of each fraction. If a few weak links are included in a strong chain it becomes weaker. Stronger links in a weak chain have little affect on the overall strength. This is why only a surfactant small concentration can have such a dramatic affect on the surface tension of a clean amine solution.



Antifoam and most liquid hydrocarbons are immiscible in aqueous solutions, and have low surface tensions. They tend to be incorporated in aqueous interfaces as small droplets, or even spread out into a thin film depending on the chemical nature of the compounds. The repulsion between soluble and insoluble compounds creates a break in the interface which is even weaker than soluble surfactant links. In the case of spreading, the surface tension measured might be the immiscible liquid alone. The result is extremely low surface tensions.

In general, extremes (high & low) in surface tension create unstable foams. Water (high) does not readily foam due to surface molecules pulling the film back into the bulk solution. Low surface tension liquid films are fragile and beak due to shear (antifoam & hydrocarbon). Stable foams are usually formed in intermediate surface tension solutions because they are weak enough to form a stable film, but strong enough to resistant local shear forces.

Another common misunderstanding is not all amine foaming incidents are cause by solution chemical contamination. Chemical and mechanical foaming produces the same flooding symptoms. The remedy for foaming symptoms is to inject the solution circuit with ANTI-foam. Adding antifoam has been the most common foaming abatement practice for two primary reasons; it relieves the symptoms on a temporary basis, and is quite easy to use. Most users also add "cheap" to the justification, but cheap is a relative

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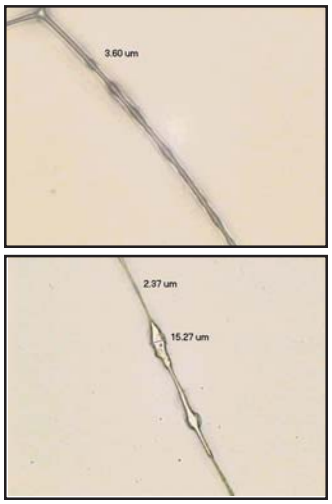
term. Injecting antifoam on a short term basis is quite inexpensive. However, over the long term its affects on the solvent and plant operation make it quite costly.



Antifoam destabilizes the froth or foam by acting on the gas - liquid interface. It has been shown in numerous studies from several industries that surfactants inhibit gas to liquid mass transfer, in some cases up to 70%. Antifoam produces the same inhibition while destabilizing the froth or foam. Although not completely understood it has been hypothesize that, where surfactants increase liquid film inhibition, antifoam may increase froth break time so much that there is not time for mass transfer to take place. When this theory was tested with MDEA in 2001 (Linga et.al., LRGCC), the solution's ability to remove acid gas was reduced by an incredible 40-50%. How much more capacity could a plant gain if the solvent were even 20% more active? Just the energy savings from reducing circulating rates and reboiler duty would be significant. When its affect on premature filter and activated carbon fouling is added, the cost of using antifoam gets quite large.

D-Foam, Inc. has developed a process that allows users to; **1.** easily treat solvents for chemical contamination, **2.** reduce their dependence on antifoam, and **3.** troubleshooting their plants at the same time. Foam causing and enhancing contaminants are removed by taking advantage of the surfactant's natural tendency to stick to gas - liquid interfaces, i.e., gas bubbles. The surfactants generate the backbone of the foam structure, and are subsequently removed as the unit removes the foam. As the foam causing contaminants are removed from the solution the plant's foaming symptoms subside.

One of the operating features of this device is its demonstration of the solvent's on-line foaming tendency while producing foam. Since it is more efficient than the plant at generating foam, it is also much more sensitive to changes in foaming tendency. Surfactant concentrations well below symptom causing levels are measurable. From monitoring and troubleshooting standpoints, even minute foaming contaminant ingress and/or generation from degradation become detectable.

Features & Benefits

- no disposables like filters, activated carbon, resins, or membranes
- no required pretreatment, chemical additives, or regeneration
- slip stream operation for ease of installation to plant piping bleeders
- low operating costs - the only consumption is power for the pumps.
- low maintenance costs - the only moving parts are centrifugal pumps
- not solvent or contaminant specific - whatever is causing the solution to foam is removed with the foam
- can operate rich or lean without safety concerns because there is no reason to access internals
- minimum clean waste generation so it is environmentally friendly, with plant waste pit disposal
- portable - the unit is trailer mounted for movement between plants or trains

SigmaPure Operation

The contaminated solvent enters the unit near the top of the foam induction section where it encounters a continuous cascade of bubbles. The surfactants stick to the bubbles and are incorporated in the foam being generated. As the concentration of surfactants build at the interface, the foam propagates up through the drying section. The clean solvent incorporated in the foam structure drains to equilibrium with gravity. A series of coarsening internals causes the foam to dry even more creating "super dry" foam to absolutely minimize solvent loss and waste generation. The dry foam enters the stripping section where the liquid and

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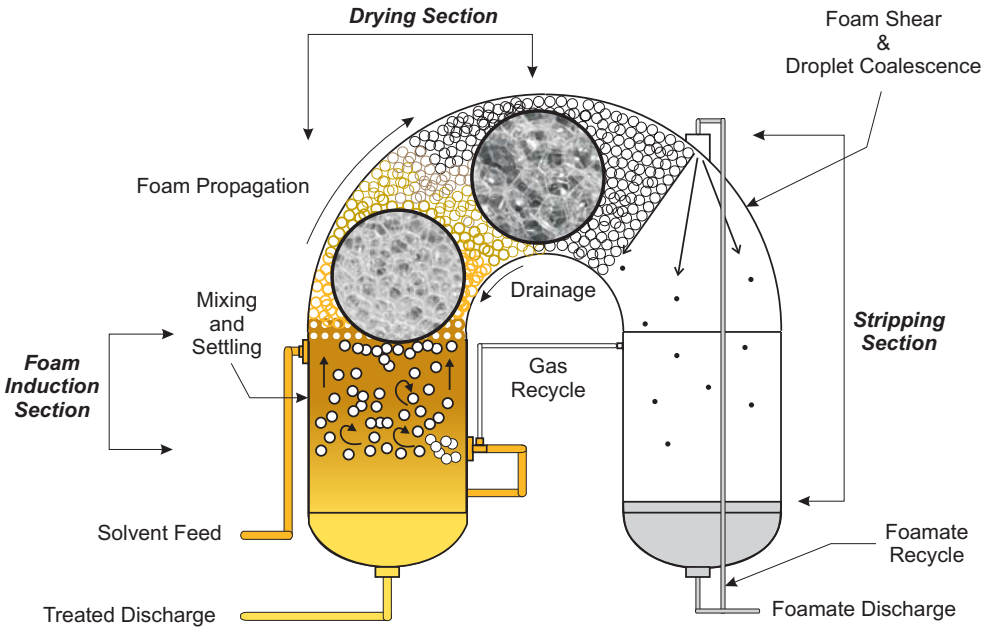


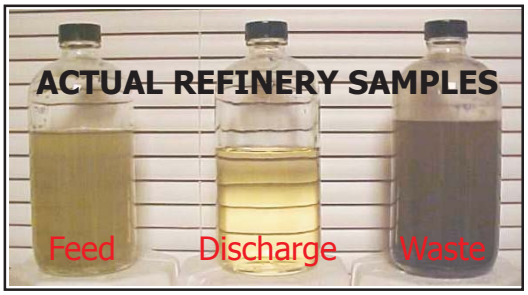
gas fractions are separated by a liquid spray of recycled waste. The gas fraction is recycled through an eductor to the foaming section where it produces more mass transfer area for surfactant adsorption.

Treating with SigmaPure

The SigmaPure System was designed to operate essentially unattended, normally requiring only periodic operator inspection. It can be used to treat any amine solution, and does not target any specific contaminant over another. If a contaminating compound causes foaming, the SigmaPure system will remove it. The photo (right) shows actual refinery samples of a SigmaPure application. The color and clarity improvements were caused by suspended solids being incorporated in the foam structure and removed.

Amine Solution "Foamers" We've Found (so far)

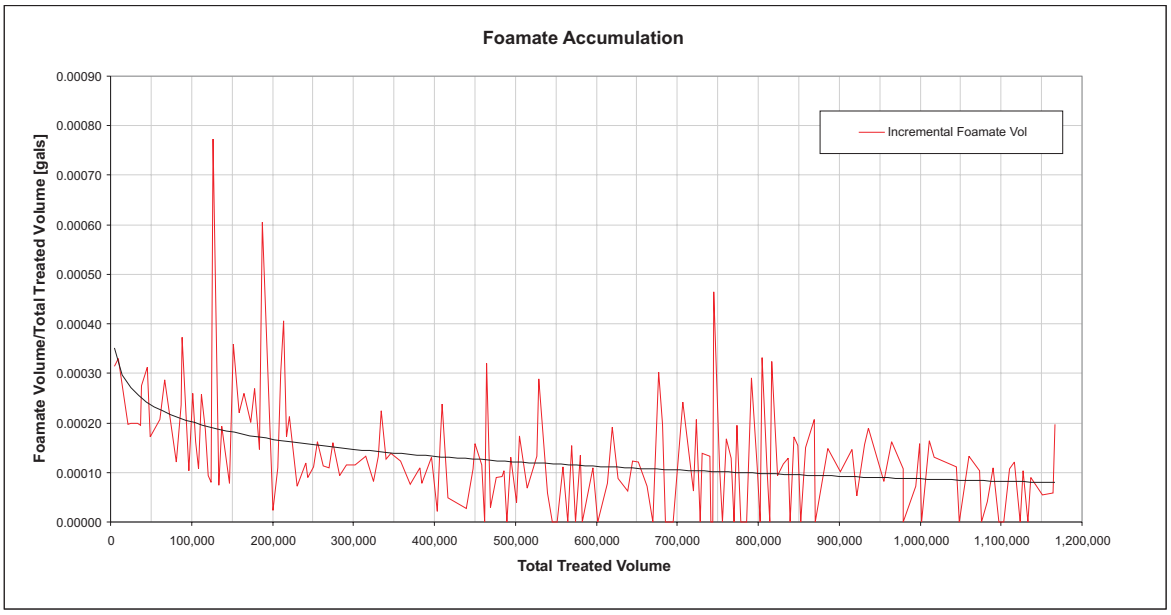
The actual foam causing contaminants found in sweetening solvents include; heat stable salt anions, carboxylic and high mol. wgt. fatty acid degradation and polymerization compounds (HSS & residue precursors), ethoxylated alcohols from antifoam degradation, glycols, and soluble aliphatic hydrocarbon from liquid hydrocarbon contamination. This does not include the myriad of solid contaminants that enhance foaming.



Troubleshooting with SigmaPure

One of the benefits of on line, continuous treating for foaming contaminants is SigmaPure's use as a troubleshooting tool. No other on-line device we know of, including instrumentation, can show foaming properties of a recirculating solution more directly or with higher resolution than SigmaPure. The SigmaPure system's sensitivity to solution foaming is greater than the plant's. This means that the SP unit removes foam causing contaminants even after the plant's foaming symptoms are long gone. It also means that changes in solution foaming tendency can be measured without experiencing upsets. Since the unit is constantly removing surfactants that either enter or are being generated by the plant, a constant "sub critical" view of the solution, hence the plant's, health can be made in real time.

An actual example of what on-line foaming tendency data looks like is given in the chart on page 4. The plant was experiencing 3-4 day episodes of stripper reboiler liquid level fluctuation, symptomatic of foaming. They were also seeing small volumes of liquid hydrocarbon in reflux drum despite their flash and surge drum skimmers showing no settleable hydrocarbon liquids. Microscopic examination of solution grab



samples confirmed emulsified liquid hydrocarbon droplets. The SigmaPure unit was installed; 1. to collect liquid surfactant samples for analysis, 2. to confirm actual solution foaming, and 3. to test the unit's ability to eliminate the foaming episodes. The SigmaPure unit was successful on all three counts.
The graph shows that the solution's foaming tendency was definitely trending down (black). However, since the plant's foaming symptoms stopped after the SP unit was installed, changes in the solution's tendency to foam were not apparent. Incremental waste accumulation data (red) showed that the plant was receiving frequent minor ingress spikes that the upset symptoms had indicated as larger and every 3-4 days.

Examination of the waste (foamate) showed very little liquid hydrocarbon further suggesting that the bulk hydrocarbon was not responsible for foaming. Chemical analysis of the waste (not shown) would show that there were soluble aliphatic hydrocarbon surfactants, sulfonates, and amine/antifoam degradation constituents that were probably the greatest foaming contributors. There was also a mysterious aromatic found in the foamate that suggested another ingress source.

Troubleshooting aspects of using the SigmaPure system showed ingress incidents that were not visible from existing instrumentation because the foaming incidents had been abated. It also provided liquid samples for analysis and better source definition. It confirmed that the plant was experiencing chemical foaming. It also gave the plant the luxury of time to contemplate the data while the plant was stable.

Differentiating chemical from mechanical foaming is an important troubleshooting SigmaPure aspect. SigmaPure has been able to show fabrication and design errors in new plants. It has also shown downcomer and tray restrictions in existing plants that had become so critical they had to continuously inject antifoam just to operate. In each case, the weeks of start up time and large quantities of antifoam spent chasing mysterious "solvent" problems could have been saved. In the case of internal fouling, if the SP unit had been on line the plants would have been able to save operating capital by reacting to it months in advance if it had even occurred at all.

The **SigmaPure** system removes chemical foaming agents from amine solutions, continuously, without the use of disposable internals, while requiring only modest supervision from plant personnel. It removes surfactants formed from amine and antifoam degradation, ingress, and heat stable salt/residue precursors, while leaving those solution constituents that do not cause or enhance foaming untouched. The system allows continuous monitoring of amine foaming properties under operating conditions, in real time, while removing foam causing chemical agents. In the end, whether treating for chemical surfactant removal, on line foaming tendency monitoring, or troubleshooting foaming symptoms, SigmaPure is the simplest, most trouble free answer to amine solution foaming.

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