

ANTIFOAM

WHAT IS IT? HOW DOES IT WORK?

WHY DO THEY SAY TO LIMIT ITS USE?

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Introduction

D-Foam, Inc. personnel contacted a number of gas processing plants in Texas, New Mexico, and the Canadian province of Alberta, and asked about the occurrences of foaming problems. In every case the answer was “seldom if any occurrences”. When asked about antifoam use, not a single plant was operating without it! Antifoam injection frequencies varied from once per month to continuous. A few plants even reported that amine solutions had to have an excess concentration of antifoam in order to run properly. One large gas plant in New Mexico had control loops from their differential pressure sensors to their antifoam injection pumps to facilitate their injection responses. If the tower differential pressure rose above a certain level, the pumps automatically gave the plant a dose of chemical antifoam. Chemical addition was not even an operator decision any longer.

Over the past 4 years of concentrating on amine solution foaming problems, we have been asked numerous times to explain; what antifoam is, how it works, how to tell which one and how much to use, and why occasionally it seemed to stop working. One of the disturbing things we haven’t been asked is, “if antifoam hurt the plant in any way.” For a substance to be added so frequently by so many plants there does not seem to be much known about antifoam in the gas processing industry. There is a need for an article that explains, in plain language, how gas - liquid interfaces are affected by surface active chemical compounds, especially as it relates to foaming and the use of antifoam in amine sweetening solutions.

What is Antifoam?

Antifoams are chemicals designed to prevent the formation of foam. *De-foamers* break existing foam. In the normal gas treating plant’s recirculating solution circuit, antifoaming additives are intended to act as both antifoams and de-foamers. Antifoams may be added to the solution prior to foaming symptoms occurring, but normally injections take place as a response. Antifoam that is injected eventually disburse throughout the plant’s solution inventory to prevent foam generation as the solution is agitated in stripping and absorber columns.

There are thousands of different antifoams. Anything that has destabilizing affects on foam is antifoam. The efficiency is dependent upon the bulk solution chemistry, operating conditions and surface active agents (surfactants) creating the foam. The most productive antifoams have traditionally been synergistic mixtures of hydrophobic liquids and solids. Examples classified by major constituent would include: 1. *Non-polar oils*, like minerals, silicones; 2. *Polar oils*, such as fatty alcohols, fatty acids, alkyl amines, alkyl amides; and 3. *Hydrophobic solids*, i.e., treated silica, aluminum oxide, polypropylene. These compounds almost always contain additional surfactants to enhance other properties required in the finished blend, i.e., surface wetting, emulsification, particle dispersion, or detergency. One of the confusing aspects of surfactant applications is a chemical compound that has

Table 1 Examples of Oil Field Surfactants

Surfactant Category	Type	Used In Products of Type*
Alkyl aryl sulfonates	Anionic	EB, CI
Alkyl sulfates	Anionic	AF
Alkyl ethoxylate sulfates	Anionic	AF
Phosphate esters	Anionic	CI
Quaternary ammonium compounds	Cationic	CI, BC
Fatty amine salts	Cationic	CI
Fatty acid amides	Cationic	EB
Imidazolines	Cationic	CI
Alkyl phenol ethoxylates	Non-ionic	CI, BC, EB
Alkyl poly glycosides	Non-ionic	CI
Ethoxylate-Propoxylate polymers	Non-ionic	EB
Fatty alcohol ethoxylates	Non-ionic	BC, CI, EB
Betaines	Amphoteric	CI

*Key, **AF**, antifoam; **BC**, biocide; **CI**, corrosion inhibitor; **EB**, emulsion breaker

antifoaming properties in one application might be used as an emulsion breaker in another. Table 1 lists examples of surfactants and their reported applications in the petroleum industry. At least two of the non-ionic families listed are being used as antifoams in natural gas processing applications.

The vast formulation library reflects the complexity of interfacial physical chemistry, and widespread need to control foams. Antifoam “recipes” are normally proprietary; therefore seldom published in detail. Even if the recipes were published it would be extremely difficult, given the state of the art, to distinguish which components were actually causing the antifoaming action at any given time in any particular application, hence, the trial and error application requirement.

In many ways, the art of breaking or preventing foam is as complex as its formation. Certainly it is a subject that has, and is currently undergoing intense study. There are no hard and fast rules governing the efficacy of a given antifoam formulation in any particular application. For the most part, each application is based on empirical data, usually bench level trials. There are, however, some physical and chemical factors consistent among observations made while studying antifoams and their functionality under different conditions. Factors that affect antifoam performance include:

1. *Solubility* – Most antifoams exhibit extremely low solubility in aqueous solutions.
2. *Droplet size* – The entry force required to allow the antifoam droplet to enter the bubble wall generally increases as antifoam droplets become smaller.
3. *Presence of hydrophobic solids* – Liquid/solid mixtures are usually more effective than either component used alone.
4. *Environmental shear* – Some antifoams are inactivated by too much shear. This is principally due to solid/liquid separation, and antifoam droplets being too small to bridge the bubble lamellae. Shear also plays a major role in the differences between dynamic and equilibrium surface tensions. If the interfacial area increases faster than the surfactant molecules can occupy it, the dynamic surface tension will be higher. Equilibrium surface tension represents the fully saturated surfactant film along the interfacial area. The same dynamic affects apply to antifoaming surfactants ability to occupy interfacial area.

5. *Repeated exposure to foaming* – Often, repeated exposure to foaming eventually exhausts the antifoam’s ability to inhibit formation. This is probably due to the separation of hydrophobic solids and/or reduced droplet size. (See #4. above) Multiple shake test experiments have shown that some antifoams gradually lose their antifoaming ability.

6. *Competing chemical constituents* – Other surface active chemical constituents have been found to occupy interfacial area and reduce the affects of antifoams. This is one reason why some antifoams work better in high shear environments where gas – liquid interfaces are constantly being formed, and not so well when added to existing foams. The presence of an antifoam co-surfactant may also cause inhibition.

7. *Surfactant concentration* – Higher surfactant concentrations tend to reduce antifoam effectiveness by increasing the entry force necessary to bridge the interfacial film.

8. *Dissolved salt species and concentration* – The presence of high valence metal ions reduces antifoam effectiveness. Counter-ions surround the polar ends of the surfactant molecules, reducing their electrostatic interaction with other surfactant molecules in the film.

The two antifoam types described most by gas processing plant personnel are: 1. *Silicones*, mixtures of non-polar siloxane oils and hydrophobic silica solids, 2. *Glycols or high molecular weight alcohols*, mixtures of polar oils and other high molecular weight surfactants.

Silicone Antifoams

The most prevalent types of antifoams in the gas processing industry are “silicones”. (See figure 1). The majority of these antifoams are made up of siloxane oils mixed with silica particles in varying concentrations; although some do not contain silica. Chemically, siloxane oils have long, hydrophobic “R” hydrocarbon groups attached to silicon atoms which render them very insoluble in aqueous solutions. Most silicone antifoams contain silica particles that are treated to make them hydrophobic so they will remain suspended, preferentially, in the silicone oils. The photomicrograph in figure 1 shows a silicone oil droplet with suspended silica particles. The droplet appears granular.

The synergism between the silicone oil and the hydrophobic silica particles is described as their acting as “pins”, breaking the surfactant film surface and subsequently reducing the antifoam droplet’s entry force requirement.

While the silicone family of antifoams have unquestioned antifoaming ability, there have been serious concerns with their use in gas processing systems. These concerns include: 1. their tendency to exhaust in service; 2, their potential impact on heat transfer and corrosion inhibitor function due to their surface wetting or coating tendency. Premature fouling of mechanical filters and activated carbon due to surface coating and insolubility have long been associated with the use of silicone antifoams. Most recently, mass transfer inhibition has proven to be a concern as well.

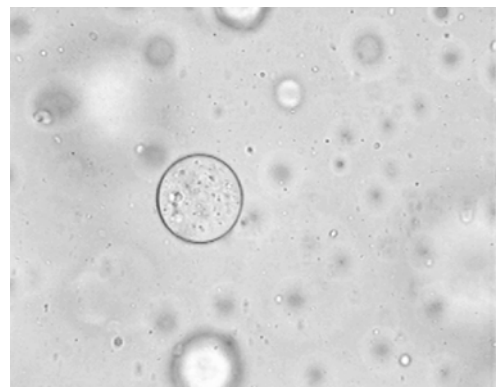


Figure 1 Silicone Antifoam

Silicone antifoams exhaust in service when the silica particles separate from the oil fraction. Interestingly, simply adding more siloxane oil revives the antifoaming ability, but is not any more costly than simply adding new antifoam.

Overdosing silicone antifoam has gained the reputation of actually creating foam. In fact, studies show that these antifoams reach a critical concentration where they do not cause foaming; but rather, simply fail to inhibit it. At elevated concentrations the antifoam gets tied up in micelle structures in the bulk solution. Once tied up in micelles, it can no longer spread on the interface, form lenses, and be incorporated in the foam's structure.

Polar Oil Antifoams

The polar oil family of antifoams combines electrochemically neutral hydrophilic moieties with long hydrophobic hydrocarbon groups. These antifoams are formulated from, and usually named some variant of: poly-glycol copolymer, polypropylene or ethylene block polymer, polyoxyethylene/oxypropylene esters of C8-C30 fatty acids, oxy/ethoxylated alcohols, and other non-ionic surfactants. As with silicone oil formulations, insolubility in aqueous solutions is the key property of these antifoams. They are most effective above their *cloud points*. Below their cloud point, some non-ionic surfactants have been shown to actually cause surfactant films to become thicker and more stable due to long range electrostatic repulsion between the monomers. Above their cloud points, studies have shown that they produce insoluble droplets that are incorporated into the interfacial films as other insoluble oils.

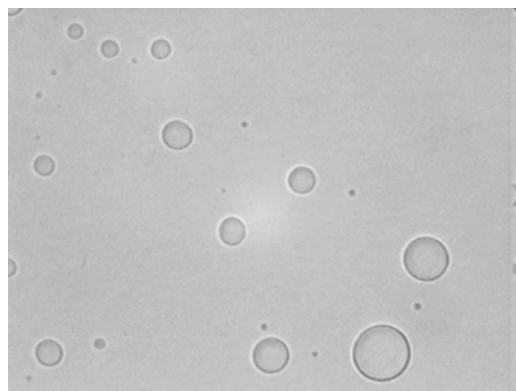


Figure 2 Polar Oil Antifoam

Non-ionic surfactants offer several other properties not found in silicone antifoams, the most obvious of which is the lack of a synergistic solid component. The micrograph in Figure 2 shows droplets of polyglycol antifoam in an MDEA solution. Note the lack of droplet granularity. This lack of a solids fraction eliminates in situ exhaustion due to separation.

Interestingly, non-ionic surfactants are also used as “foam boosters” in products like shampoos and soaps where foaminess is desirable. They reduce the oil droplets' entry into the foam films. They are normally included in the product as a co-surfactant with other surface active chemicals that have high detergency and foaming tendencies, i.e., anionic surfactants. They have also been shown to reduce the micelle stability of other foam producing surfactants, thereby sustaining the foaming tendency rather than inhibiting it.

Foaming Fundamentals

In order to understand antifoaming mechanisms a basic understanding of foam is necessary. Foam bubbles are liquid polyhedral cells encapsulating a gas (See figure 3). The *Lamellae* are the faces separating two cells. The *Plateau Border* is the thicker junction between lamellae. *Vertexes* are the junctions of four Plateau Borders.

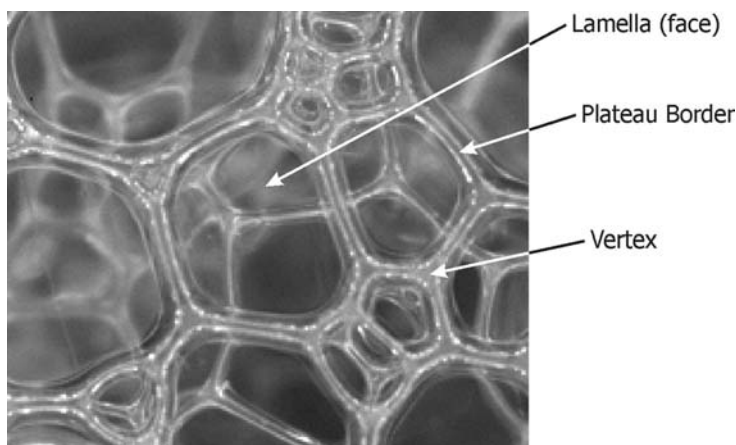


Figure 3 Foam Anatomy

The Plateau Borders and Vertexes can be thought of as the foam structure's plumbing network. Plateau Borders are continuous through the foam structure, and are the foams drainage conduit. Excess liquid in the foam structure drains, via the connecting Plateau Borders, to equilibrium between gravity and the film's capillary force. It is the foam's liquid content that gives it elasticity. As a foam structure drains the bubbles change shape from round to polyhedral, and become more rigid (see figure 4).

The surfactant film that forms the lamella is the target of fast antifoams since it is the thinnest and weakest part of the cell. The film structure is a surfactant – solution sandwich where some of the bulk solution is captured between two surfactant layers, as shown in figure 5. As the foam structure drains the lamella thins, and the two surfactant films get closer together. When they get very close, the molecules begin to repel electro-chemically. They also compress side to side along the length of the lamella. It is this electro-chemical interaction that causes the bubble structure to become more crystalline, take on a polyhedral shape, and become more rigid.

Surfactants naturally form interfacial films due to their chemical structures (see figure 6 #1). They preferentially orient toward different phases due to their chemical structures. Figure 7 shows the how the traditional head and tail graphic represents polar and non-polar moieties of a classic surfactant. The carboxyl group is the polar, hydrophilic head. The chain of methyl groups in the acid make up the non-polar hydrophobic tail of the surfactant. A more realistic graphic representation of the hydrophobic group is shown in figure 6, #2.

At low concentrations, surfactants exist as monomers in solution (figure 6 #3). They orient and form interfacial films when gas liquid interfaces are formed, e.g., bubbles rising through amine solutions. If the concentration increases, surfactants begin to orient themselves in bunches called micelles (figure 6 #4). The concentration at which these structures form is called the *critical micelle concentration*. Surfactant molecules tied up in micelles are not free to form interfacial films. The solution's foaming tendency and surface tension become more constant at concentrations above the CMC. A good rule of thumb for the CMC's of the different families of surfactants would be approximately 10^{-2} to 10^{-3} mole, at ambient temperature and low counter-ion concentration.

The irregular spacing shown between surfactant molecules in the film and micelle in figure 6 represent what happens when more than one surfactant species is present in the solution or at the gas – liquid interface. The variable spacing caused by the hydrophobic tails of the different surfactant molecules reduces the stability of both the resulting films and micelles. Solutions of mixed surfactants produce less stable films and micelles. Less stable micelles react to shear by breaking up; thereby providing surfactant monomers for film development. However, the films that are generated are, in turn, less stable. One of the strategies used in antifoam formulation is to destabilize surfactant films by including other surfactants that have very

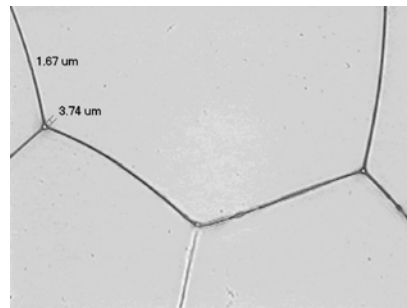


Figure 5 Drv Foam Structure

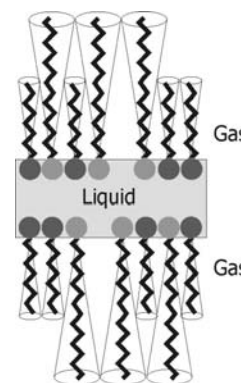


Figure 4 Bubble Lamella

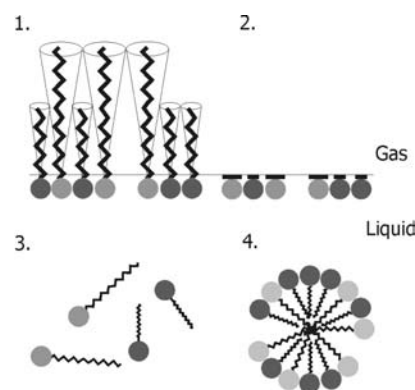


Figure 6 Surfactant Interactions

long hydrocarbon tails which create large intermolecular distances between surfactants producing interfacial films.

Surfactants normally decrease the interfacial or *surface tension* of aqueous solutions. Surface tension is a measure of the molecular interaction at the gas – liquid interface. Clean water has a surface tension of approximately 72 dynes/cm². A clean, operating, 40% MDEA solution sampled down stream of the surge drum might have a surface tension in the 55 dyne/cm² range two days after an antifoam injection. If the same sample were taken a few hours after the injection the surface tension would probably be different.

In aqueous solutions, lower surface tensions normally mean higher surfactant concentrations at the interface. However, surface tension data taken alone can be misleading. For example trying to predict a gas treating solution’s foaming tendency due to surfactant contamination cannot be done with surface tension alone. Some surfactants, e.g., antifoams and liquid hydrocarbon, reduce the solution’s foaming tendency while also reducing surface tension. Since these compounds are surface active, they will affect the surface tension in the same way a foam causing surfactant would. Another expensive example of misinterpreted surface tension data would be assuming activated carbon exhaustion due to low surface tension readings.

Foam Destruction Mechanisms of Antifoam

The most widely agreed upon mechanism of antifoaming action is summarized in figure 8.0. Emulsified droplets of insoluble oil suspended in a solution enter the lamella formed by surfactant films as a gas bubble is displaced above the bulk surface. The force required for the droplet to be incorporated into the film is known as the *entry barrier*. Studies have shown that the suspended hydrophobic solids in the antifoams reduce the droplet entry barrier into the film thereby making them more efficient.

The foam structure begins to drain immediately after forming causing the lamella to thin. The incorporated antifoam droplet bridges across the film creating an oil “lens”. The droplet is stretched as the film contracts, and eventually ruptures breaking the bubble. This action takes place in only a few seconds, and is characteristic of “fast” antifoams.

If the oil droplet fails to enter the lamella and destroy the foam, it normally becomes trapped in the foam bubble’s Plateau borders as the excess liquid in the foam

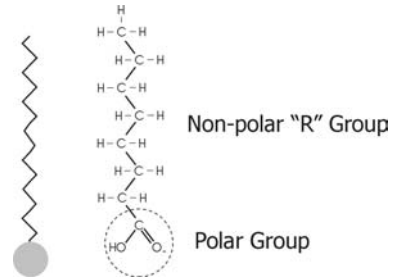


Figure 7 Surfactant Morphology (carboxylic acid)

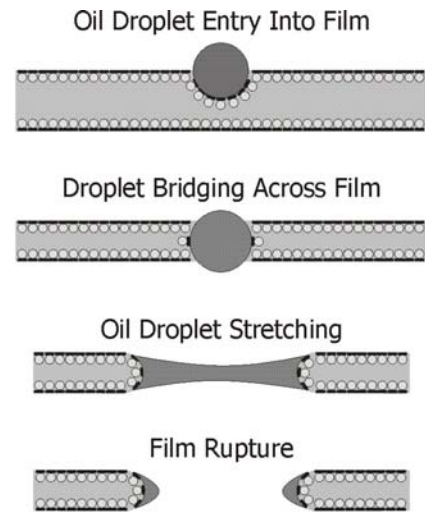


Figure 8 Antifoaming Mechanism

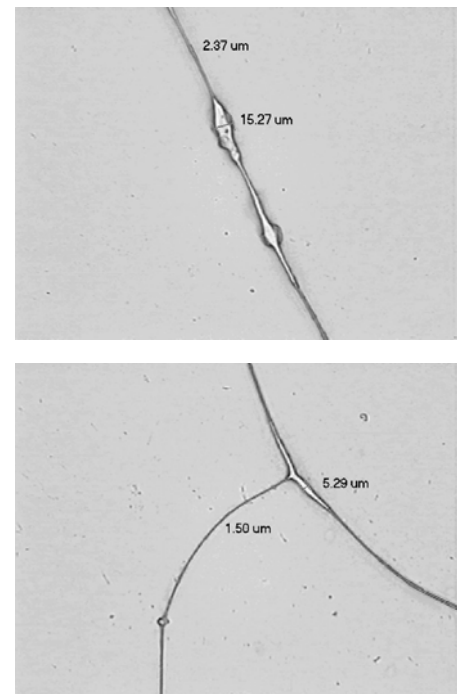


Figure 9 Antifoam trapped in Bubble’s Plateau Border (top) and Vertex (bottom)

structure drains (see Figure 9). If the capillary pressure becomes greater than the required entry barrier force, the droplet may enter the lamella and break the foam. This is characteristic of “slow” antifoams.

Why limit antifoam use?

Most of the manufacturers and suppliers of amine solutions recommend short term and limited use of antifoams with their products, but seldom give adequately convincing reasons other than addressing the cause of foaming. As was described in this article’s introduction, most plants do not consider foaming to be a problem as long as antifoam injection gets them to the next operating day. The manufacturers and suppliers are right. If antifoam has to be added to the solution, the plant has a problem. The following are a few consequences of adding antifoam on more than an occasional basis:

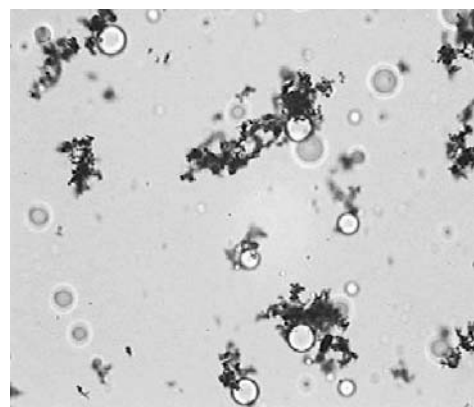


Figure 10 Antifoam/Solids Agglomerate

1. Any non acid gas absorbing foreign chemical species that competes with an amine molecule’s position at the interface of gas to liquid mass transfer area has to reduce the solution’s acid gas removal efficiency. Surface active chemical compounds naturally accumulate at these interfaces. Studies have confirmed gas to liquid mass transfer inhibition caused by surfactants. One recent study that included antifoam as a surfactant showed a 55% reduction in MDEA efficiency. Studies have also shown surfactants’ ability to affect heat transfer as well.

2. Studies have even shown that some antifoam formulations become inactive with increased concentration.

3. Antifoam does not remove or chemically inactivate foam causing surfactants. It only temporarily reduces the stability of the foam structures they produce.

4. Activated carbon adsorbs large insoluble organic molecules like hydrocarbon condensate. The larger, and more branched the molecular structure, the more efficiently they are adsorbed. It has long been known that activated carbon removes silicone antifoams quite efficiently. Studies have also shown that it adsorbs non-ionic antifoams as well.

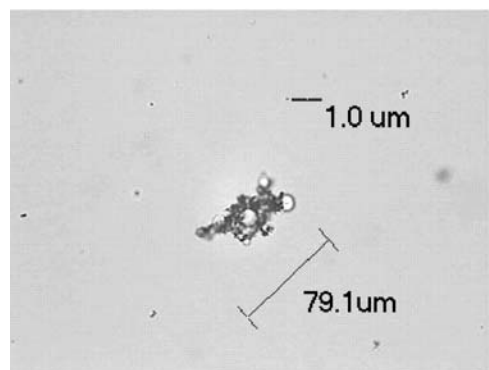


Figure 11 Antifoam/Solids Agglomerate

5. Figures 10 and 11 are photomicrographs of antifoam bubbles adsorbing suspended iron sulfide particles, and forming large agglomerates in amine solutions sampled from operating gas plants. They show how antifoam droplets can prematurely plug activated carbon beds and mechanical filters even if the droplets would pass through without being adsorbed.

6. Antifoams, being surfactants themselves, affect surface tension measurements. Use of manufacturer or laboratory surface tension data to indicate the presence of soluble, foam causing surfactants becomes impossible.

7. The presence of antifoam in the system severely inhibits the differentiation of mechanical versus chemical causes of foaming symptoms since both are affected to some degree by the surface tension reduction.

Conclusion

Process foaming is a problem that requires immediate action for operating plants in all industries. This is especially true for operators of amine sweetening processes in natural gas plants and petroleum refineries. Learning as much as possible about the nature and affects of chemical additives used in these plants should be the goal of everyone involved. The injection of chemical antifoams into recirculating amine solutions is an everyday practice for many gas treating plants. It should be well understood that, although antifoam may offer a short term operating remedy, there are potentially severe consequences from its misuse. The need to inject antifoam on anything other than an occasional basis is a symptom of a problem, not a solution.

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