

AICHE PRESENTATION

"THE TECHNOLOGY OF DEFOAMERS IN PHOSPHORIC ACID SERVICES"

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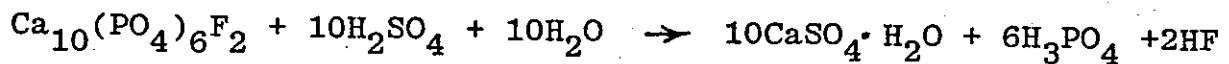
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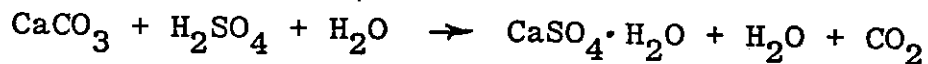
DEFOAMER HISTORY

Since the early 1900's, the fertilizer industry has been producing phosphoric acid by the acidulation of phosphate rock with sulfuric acid. During this period, the phosphoric acid producers have been adding foam control agents to their processes to increase production rates, reduce pump cavitation and reduce P₂O₅ losses. This reaction of phosphate rock and sulfuric acid generates large quantities of stable foam because of the substantial amount of calcium carbonate and other organic impurities that are present in the phosphate rock. The products of this reaction are phosphoric acid, calcium sulfate, hydrofluoric acid, water, and carbon dioxide, which is evolved as a gas.

The principal reaction in a wet-phosphoric acid process is:



The main reactive impurity in sedimentary phosphate rock is calcium carbonate, which reacts as follows:



During the 1920's, crude fats and oils were used in large quantities to control the foam produced in the small batch production units of the day. Many of these production units used as much as 25 pounds of fatty acid per ton of P₂O₅. The 1930's - 40's saw the first of many continuous production units in which defoamers were used to increase production rates. The defoamers used during this period were primarily vegetable oils and acids. The larger production units that were introduced in the fifties and sixties necessitated the invention of more complex and sophisticated phosphoric acid defoamers. These new defoamers consisted of surface active derivatives of fatty acids such as esters and amides and when combined with low cost fatty acids were termed "Blended

Defoamers". These blended defoamers were the work horses of the fertilizer industry for twenty years with many of the production units using as little as 4 to 5 pounds per ton of P_2O_5 . The early seventies saw even more complex blended defoamers and the introduction of new water soluble "Sulfonated Fatty Acid Defoamers". These sulfonates were chemically stable under strongly acidic conditions, like phosphoric acid manufacturing, and offered benefits of water solubility and reduced damage to the rubber linings of evaporators and transfer lines. The early 1980's saw about one-third of the industry change to "Emulsion Defoamers". These products generally contain the same types of surface active agents that were used in blended defoamers except they were introduced into the phosphoric acid plant as oil-in-water emulsions. These products offered improved cost performance for many chemical plants. Today, about 40% of the industry is thought to use emulsion defoamers, 40% sulfonated defoamers and 20% blended defoamers. The defoamer consumption for the industry is about 5 pounds per ton of P_2O_5 with some plants averaging less than 2 pounds per ton. This decreasing consumption trend has been the result of both better plant controls and more effective defoamers.

WHY SOME FOAMS ARE STABLE

To gain a better understanding of how defoamers reduce foaming conditions, one must first look at why certain systems generate stable foams. Foams are agglomerates of gas bubbles separated from each other by their liquid films. In order for these foams to be stable, three basic requirements are necessary. First of all, the system must be liquid. Secondly, a gas must be introduced into the system or formed as part of a reaction. Finally, there must be a contaminant present in the liquid medium to provide stability to the foam. In wet phosphoric acid manufacturing, all of these basic requirements are present. The process occurs in a liquid medium with water being added both to the reaction vessel and being generated in the chemical reaction itself. There is a large amount of carbon dioxide gas generated and there are many organic contaminants present as evidenced by the dark color of the acid.

It is important to understand that pure liquids cannot sustain a stable foam. This principle is so universal that one can estimate the purity of drinking water by watching the bubbles that form. If stable bubbles form, the water is contaminated and not fit to drink. In the manufacture of phosphoric acid, it is obvious that we are not dealing with a pure system. Sedimentary deposits of phosphate rock generally contain organic matter of both plant and animal origin. There is no detailed analysis of this organic

material, but it is generally thought to consist of a mixture of high molecular weight compounds of varying composition, depending on the rock that is mined. High temperature calcining of the phosphate rock can greatly reduce the stabilization effects these impurities have on the foam generated in the phosphoric acid process.

There are two general classifications of foam types. The first is designated "kugelschaum" or widely separated spherical bubbles. The second classification is designated "polyederschaum" which consists of bubbles that are nearly polyhedral in shape, with thin films of liquid in between. It is this polyhedral foam mass that rapidly forms in phosphoric acid attack systems. The major forces that influence this formation and stability are capillary action (surface tension and interfacial tension), viscosity, temperature, gravity and mechanical actions.

To date, a complete thermodynamic description of foam has not been written and therefore, the relationships of the above forces are not completely understood. However, it is possible to look at each force individually and gain some understanding of how they work in stabilizing foam. Capillary action and increases in viscosity are forces that stabilize foam structures. Gravity and mechanical action are forces that weaken or destroy foam. Other system factors such as temperature, pH, and specific gravity will produce changes in surface tension and viscosity that can weaken or strengthen foam structures.

In a stable foam, the normal drainage of liquid from the foam film caused by gravity is offset by the restoration of the lost liquid by what is called the "Marangoni effect". This effect is a measure of the ability of a foam surface to heal itself when subjected to mechanical shock or other destabilizing factors. Where stresses on the foam film are the greatest so is the surface tension. This force will cause the motion of relatively thick layers of underlying fluid to balance the downward flow of liquid. This balancing of fluid increases the surface elasticity and stability of the foam.

The viscosity of the liquid medium will also affect the drainage rate of liquid from the foam film. If viscosity is very high, drainage is greatly hindered and the lifetime or stability of the foam is greatly increased.

In phosphoric acid manufacturing, the organic contaminants, the high viscosity of the liquid slurry and the entrapment of calcium sulfate crystals in the foam film combine to produce a very stable, slow draining foam structure.

HOW DO DEFOAMERS WORK

One of the main measures of the effectiveness of a defoamer is surface tension. Strictly speaking, surface tension (dynes/cm) is the force (dynes) required to extend the surface of a liquid by 1 cm or, the energy (ergs) required to increase the area of the surface by 1 cm². In order for a defoamer to be effective, the surface tension of the defoamer must be less than the combined surface tension of the liquid medium and the surface tension of the interface between the defoamer and the liquid. If this condition is met, the defoamer will migrate to the liquid surfaces and counter the stabilizing effects of the Marangoni effect. If this condition is not met, the defoamer will not rupture bubbles.

This migration of defoamer molecules can also be said to create areas of low free energy on the surfaces of the foam structures. The liquid in the foam film will seek the area of highest free energy. Since the continuous liquid phase represents the highest free energy in the system, the liquid in the foam film will drain more rapidly. In effect, the liquid will try to escape from the defoamer causing the surface of the bubbles to become thinner. As this draining of the surface progresses, the bubble becomes increasingly less stable until it ruptures. This phenomenon is known as the LaPlace Effect.

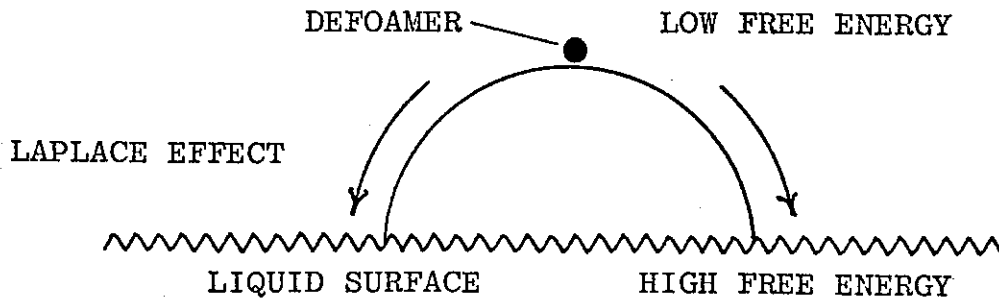
SURFACE TENSION (γ)

$$\gamma_D < \gamma_L + \gamma_{DL}$$

WHERE: γ_D = SURFACE TENSION OF THE DEFOAMER

γ_L = SURFACE TENSION OF THE LIQUID

γ_{DL} = SURFACE TENSION AT INTERFACE OF THE DEFOAMER
AND THE LIQUID



It is this principle that Sulfonated Defoamers and other highly surface active products take advantage of in controlling foam. These products also are antifoaming agents, that is, causing consolidation of gas bubbles before they reach the surface. This helps to reduce entrained gas that can cause pump cavitations and can reduce or eliminate defoamer usage in down stream operations.

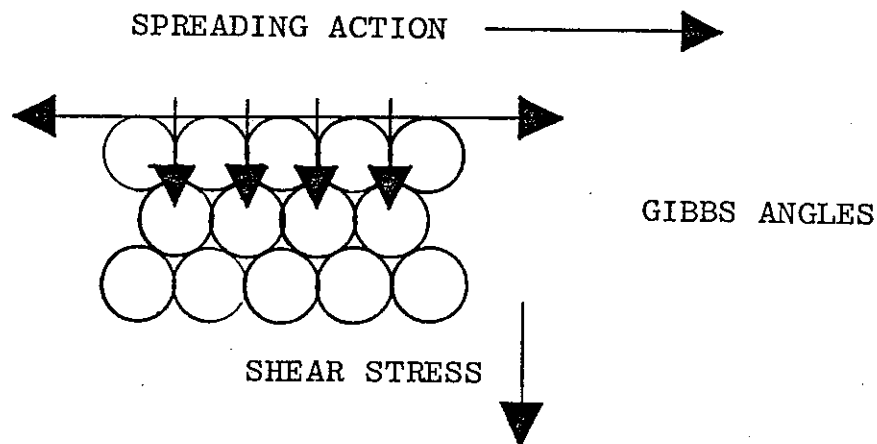
Another principle in determining the effectiveness of defoamers is particle size. In order for a defoamer to spread across the surface of a liquid, the surface tension of the liquid minus the surface tension of the defoamer minus the surface tension of the interface between the defoamer and the liquid must be less than zero. If this condition is not met, the defoamer will not disperse in the liquid medium. When this condition is met, the particle size of the foam-inhibiting agent will be reduced to a degree where spontaneous spreading over the surface of the foamy liquid will take place. The spreading of these small particles of defoamer will cause mechanical action to rupture the foam film which in turn generates a shearing stress to the liquid beneath. This spreading of the defoamer will cause mechanical action to rupture the foam film which in turn generates a shearing stress to the liquid beneath. It is this shearing stress that causes the foam column to collapse in a chain reaction. After the film ruptures, the defoamer is returned to the liquid as a dispersion of small droplets, which can perform their film-breaking function again. It is this effect that blended defoamers and emulsion defoamers utilize in defoaming phosphoric acid attack systems.

Particle size = (\mathcal{S}) Spreading

$$\mathcal{S} = \gamma_L - \gamma_D - \gamma_{DL} < 0$$

Mechanical action ruptures foam film

Lateral flow communicates shearing stress to the liquid beneath



HOW DEFOAMERS ARE MANUFACTURED

Blended defoamers are blends of fatty acids (mostly tall oil derived), or petroleum based products combined with various fatty acid derivatives such as esters and amides. The most common esters are formed by reactions of tall oil fatty acids with alcohols or glycols. The fatty amide components are formed by reactions of tall oil fatty acids with various ethylene amines or alkanolamines. These different components of the blended defoamer are usually combined in a mix tank according to the prescribed formulation and shipped in bulk to the chemical plants. These products are relatively easy to make with consistent performance.

Emulsion defoamers contain many of the same compounds that are used in blended defoamers. These products, usually sold as 25-35% active emulsions in water, contain such active ingredients as fatty acids, fatty acid esters, fatty amides, and various emulsifiers. Some of the common emulsifiers that are used are fatty acid soaps, ethoxylated alcohols and sulfated alcohols. These emulsions require significantly more agitation to produce, and certain formulations will require the use of homogenizers or colloid mills. Emulsion defoamers will also be more difficult to produce on a consistent basis since emulsion viscosity and stability can be affected by very minor changes in raw materials or by seasonal variations in temperature.

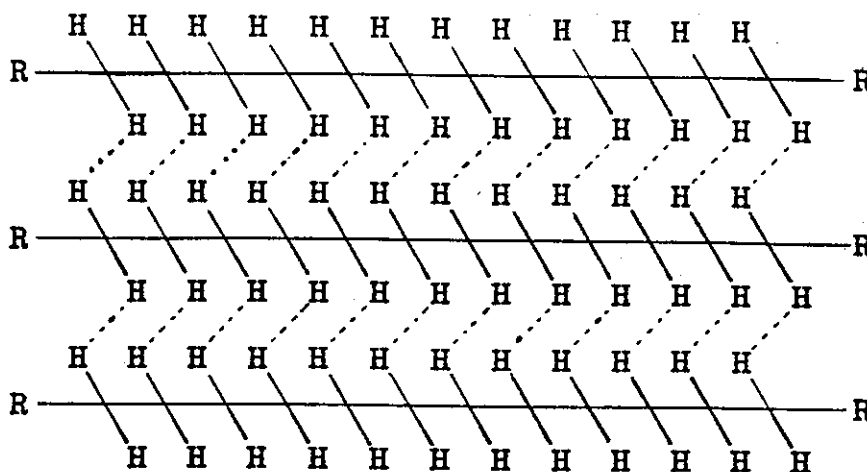
Sulfonated defoamers are manufactured by the reaction of SO_3 gas with oleic or linoleic fatty acids in a thin falling film reactor. These reactors are run on a continuous basis and produce consistent sulfonated surfactants. Sulfonated fatty acids have a true carbon - sulfur bond that is chemically stable under hot, acidic conditions. Sulfated fatty acid defoamers, produced by the reaction of fatty acids with sulfuric acid, are not stable in phosphoric acid and will hydrolyze back to free fatty acid. Both of these types of products are water soluble and are usually sold as 25% to 50% active liquids.

WHY DEFOAMERS SWELL RUBBER

The fertilizer industry has used rubber linings in its evaporators, transfer lines and many of its acid storage vessels for many years to reduce corrosion problems. These rubber linings have proven over the years to be expensive to maintain because many of the defoamers used in the industry attack rubber, causing the surface of the rubber linings to swell.

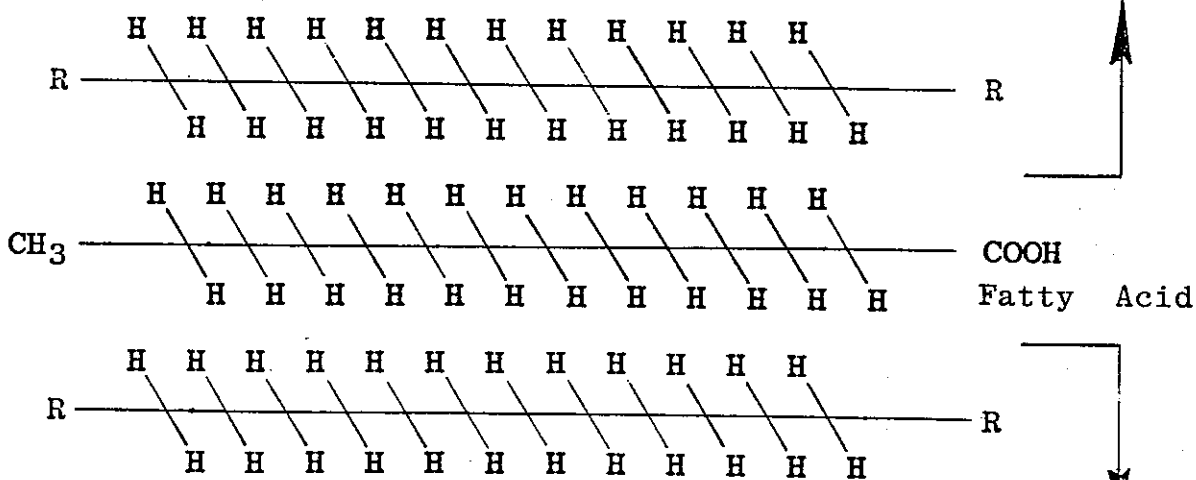
To understand why rubber swells, one needs to first examine the rubber molecule itself. Rubber is a series of extremely long carbon chains held together by weak Van der Waal forces. It is the layer upon layer of these long carbon chains, held together by rather weak attractions that give flexibility to rubber.

Rubber Layers



High molecular weight carbon chains

Held together by weak Van der Waal Forces (---)



Rubber layers separated by fatty acid molecule

Defoamers that contain fatty acids, petroleum products, and most fatty acid derivatives are non-charged and non-polar, as is rubber. Since these products are not soluble in phosphoric acid, they have a strong desire to migrate from the acid medium to the surface of the rubber. Once on the rubber, these molecules, which also contain long carbon chains, act as the agents to dissolve the weak forces that hold the molecular layers of the rubber together. When this happens, the rubber surface begins to swell. When constant attack

of the rubber continues over a long period of time, the fatty acid molecules continue to penetrate deeper into the rubber layers until significant damage to the rubber lining results.

All of the defoamers on the market today attack rubber to one degree or another. Blended defoamers are usually the most damaging to rubber because they contain high concentrations of long chain fatty acids. Emulsion defoamers exhibit about one-half the rubber swell rate of the blends due to the reduced amounts of fatty acids being introduced into the phosphoric acid by these lower active products.

Sulfonated defoamers do not attack rubber to a significant degree because of their considerably high level of solubility in the acid medium. Sulfonated fatty acids are highly charged and polar and are therefore soluble in the phosphoric acid that is also highly charged and polar. Because of this solubility, migration to the rubber surface is greatly reduced. Sulfated fatty acid defoamers, due to their lack of stability in acid, will revert to free fatty acid that will attack rubber in a similar manner as the blended defoamers.

DEFOAMER TECHNOLOGY IN THE FUTURE

As the mining industry in Central Florida moves further south, the increased $\text{CaO:P}_2\text{O}_5$ ratio will not only cause higher sulfuric acid consumption, it will cause increased foaming conditions. This will lead to increased demands on defoamers to control foam, prevent pump cavitation and minimize evaporator losses. The chemical plants processing this southern rock will probably find it mandatory to add defoaming agents at multiple points throughout the processing plants. Higher defoamer costs are almost assuredly going to be experienced.

To help the industry control this increased foaming of phosacid, the defoamers of tomorrow will in all likelihood fall into two categories. The first category will be low cost emulsion defoamers that, due to their cost, can be added in substantial quantities at

multiple locations. The second category will be composed of more complex products that exhibit improved surface tension reduction. The suppliers of defoaming agents to the phosphate industry are continually investigating new products to improve the competitive edge of our industry in the world market.

In order to bring new products to this industry, we will need to continue to work together in the testing of new ideas and products. The producers of phosphate chemicals and the suppliers of foam control agents can and must develop improved cost performance products for the many problems we face in the coming years.

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