INTRODUCTION

Unwanted foaming is a serious problem in many industrial plants. Foam problems include: safety hazards, waterway pollution, process contamination, reduced process output, restricted oxygen uptake in aeration basins, and public relation concerns. Foaming is caused by excessive turbulence, or \textit{in situ} gas generation and can be minimized with proper plant design. While plant design can minimize foam, it does not always eliminate it, and antifoam chemical is needed. Antifoams are used in applications needing smooth flowing liquids such as industries involving: latex paints, paper making, textiles, ceramics, and lubricants. Also, industries using distillation columns such as oil refineries and alcohol producers have definite foam control needs.

With increasingly stricter environmental discharge permits, the need to reduce hazardous chemical discharge becomes more important. Formulating 'greener' products and increasing product activity reduces hazardous chemical discharge. Increased activity is accomplished by using defoaming synergisms, and reducing or using cleaner oils. Synergisms are the result of interactions between two or more defoaming chemicals to greatly increase the bubble coalescence rate. Utilizing a sophisticated feed control system is the third way to reduce antifoam chemical discharge and ensure that antifoam is only fed when chemical is required.

Pollution prevention is of concern to many governmental agencies and legislative bodies across the country. This is evidenced by pending or recent legislation, such as: the Massachusetts Toxic Use Reduction Act, The Great Lakes Water Quality Initiative, California Proposition 65, etc. Wastewater antifoam chemicals are added directly to discharge streams to control foaming on public waterways. Process streams also affect plant effluents, since process residuals eventually reach the waste treatment plant. For example, paper mills have eliminated process chemicals that contain any dioxins or dioxin precursors. Also, due to regulatory and/or environmental pressures, plants have had to change production processes to facilitate wastewater treatment. This is evidenced by paper mills changing their bleach process to facilitate ACX reduction. For these reasons the composition of added chemicals, including antifoams, is very important.

BACKGROUND

Foams are thermodynamically unstable. Energy input in the form of turbulence provides energy to keep the foam from collapsing. Impurities that stabilize the air/water interface are needed because pure water cannot foam. These impurities lower the surface tension of water. Pure water has a surface tension of 72 ergs/cm$^2$, where ergs is a unit of energy; therefore, to increase the surface area by one cm$^2$ requires 72 ergs of energy. Foaming surfactants will lower the surface tension, making it easier to increase surface area. A foaming liquid has
more surface area than a liquid at equilibrium and it takes energy to create this excess surface area. Also, the smaller the foam's bubbles, the greater the foam's total surface area. Comparing the surface area of one large bubble to the surface of many small bubbles occupying the same total volume, we see that small foam bubbles have much greater surface area.

<table>
<thead>
<tr>
<th></th>
<th>Single Large Bubble (radius=0.5 inch)</th>
<th>Many Small Bubbles (radius=0.005 inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Bubbles</td>
<td>1</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Total Volume</td>
<td>0.52 inches$^3$</td>
<td>0.52 inches$^3$</td>
</tr>
<tr>
<td>Area per Bubble</td>
<td>3.14 inches$^2$</td>
<td>0.000314 inches$^2$</td>
</tr>
<tr>
<td>Total Surface Area</td>
<td>3.14 inches$^2$</td>
<td>314 inches$^2$</td>
</tr>
</tbody>
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It takes energy to create this extra surface area, and excess surface area is excess foam. Foaming agents work because they reduce the surface tension making it easier to create foam. Less energy is needed to create the same amount of excess surface area.

Once a bubble has formed, it needs to be stabilized, since it is thermodynamically unfavorable to have the increased surface area. The natural course of events is for the bubble interface to drain and rupture. When two foam bubbles come together they drain then rupture, and finally coalesce. There are several mechanisms that stabilize foam.

Air bubbles that comprise foam are created by turbulence as the liquid passes through pumps, weirs, etc. and from fermentation or neutralization processes producing gas bubbles. In many plants, the rate of bubble production is constant - due to the inherent turbulence built into the system. Expensive capital improvement is often the only way to remove the inherent turbulence. Mechanical devices can be used to reduce foam and chemical discharge. These devices function by decreasing the rate of bubble production (reduce turbulence), or by 'popping' the bubbles. To keep plants profitable, the process flow rate must be high, meaning foam generating turbulence is unavoidable and antifoam chemicals become imperative. Antifoam chemicals function by increasing the rate of bubble coalescence, reversing the effect of the foaming surfactants.

Foams develop when a foam stabilizing surfactant impedes the touching of two bubble interfaces. Without these foam stabilizing surfactants, the lamella quickly drains to the plateau border allowing the bubbles to touch and coalesce. The lamella is the liquid region between two air bubbles while the plateau border is a region between three bubbles. Foams are stabilized by several mechanisms such as slow lamella drainage and lateral or 2-D diffusion of the foaming surfactant. Foam breaking is the result of lamella drainage, allowing two bubble interfaces to touch and coalesce. Lamella drainage creates a convective flux that pulls adsorbed surfactant molecules from the interface. This temporarily creates an area of reduced surfactant concentration and higher surface tension. A surface tension gradient is
formed which will oppose the flow of liquid away from the interface, that is, slowing lamella drainage. Figure 1 illustrates how this gradient drives 2-D diffusion of foaming surfactant along the interface and restores surfactant concentration or 'heals' a bubble's air/water interface. The faster a foaming surfactant can diffuse along the interface, the less time there is for bubble collapse. This is the Marangoni Effect.3

ANTIFOAM MECHANISMS

Common antifoam mechanisms are: bridging/lamella penetration, duplex film formation, adsorption of foaming surfactant, high contact angle particulates.4 Various defoaming mechanisms are used by nonhazardous chemicals such as: stearic acid, polypropylene glycol, and hydrophobic particles. On the other hand, oils are very effective defoamers and removing them usually degrades performance. One reason is that foam can be stabilized by foaming surfactant micelles, blocking the lamella. These micelles form an orderly micro-structure that impedes water drainage. Oils swell these micelles, destroying the orderly micellar structure, allowing the lamella to drain.5 This is illustrated in Figure 2.

Combinations of defoaming chemistries can be used to reduce antifoam chemical dosages. These antifoam combinations, or synergisms, exhibit greater than additive bubble coalescence rates, and can sometimes be explained using combinations of antifoam mechanisms. An oil/hydrophobic particulate defoamer can be viewed as increasing in effective particle size due to an adsorbed oil layer.6 Lamellar penetration depth is increased, meaning that bridging between bubbles occurs faster, allowing for faster bubble coalescence. This synergism can also be used to explain why combinations of immiscible antifoam chemicals can reduce antifoam chemical usage(or increase antifoam activity). For this synergism, the two immiscible surfactants actually associate in water forming a complex with a greater penetration depth than the individual oils. This mechanism is presented in Figure 3.

ANTIFOAM COMPOSITION

Antifoam formulations are either: oil-based, water-extended (an oil-based with water replacing some oil), or water-based. Oil-based antifoams use hydrocarbon oils derived from petroleum to package antifoam actives. Advantages are quick kill and low temperature application. These formulations tend to be 'universal' antifoams - at high enough dosages. They usually work by a duplex film mechanism, and unfortunately tend to produce visible oil sheens, pollute surface waters, and increase BOD loadings to the aeration basins. Additionally, the inexpensive hydrocarbon oils used in many antifoam formulations tend to contain hazardous compounds as impurities. An example important to the paper industry is oil that contains dioxin precursors. Environmental regulations are making it difficult to justify using oil-based formulations in many processes. Unfortunately, it is difficult to remove oil from antifoam formulations without reducing performance, or increasing chemical costs, but the effect of regulations are making it increasing more expensive to use oil-based antifoams.

Water-extended antifoams are derived from oil based formulations by replacing some oil with water and adding product stabilizers. These have the advantage of quick foam kill and less
oil discharged into the environment. While a water-extended formulation discharges fewer chemicals, it still uses some oil that reduces but does not eliminate the environmental problem.

Water-based antifoams work very well from an environmental standpoint, since antifoam actives are packaged using water. Since oil is not used, the effectiveness of water-based formulations is not as universal. Water-based antifoams have a distinct environmental and commercial advantage over oil-based formulations, since the use of expensive oil is eliminated. Water-based antifoams are environmentally friendly, so fewer pounds of hazardous chemicals are discharged. Also, water-based formulations lower BOD loading to the waste treatment plant. However, there are practical problems with water-based antifoams, such as higher viscosity and limited usefulness at lower temperatures.

**FEED CONTROL SYSTEMS**

Dosage control systems are used to minimize antifoam chemical usage. A reliable foam detection system is required. A fouling-resistant foam probe is needed to detect foam, without giving false readings, with the detectors able to automatically control antifoam feed pumps. Feed systems consist of pumps and pipes or hoses that distribute antifoam chemical.

Adding antifoam chemical when foaming is nonexistent is another way of wasting chemical. When feasible, an automated feed control system has minimal operator involvement. With the use of automated level probes, even antifoam chemical resupply is automated. This setup has several benefits:

1) Operator time is freed for other duties.
2) Antifoam use is optimized - minimizing environmental discharge.
3) Container disposal costs are reduced.

How the feed control system applies the antifoam chemical can be another source of excess chemical use. Since antifoam chemicals tend to be water insoluble, the products have a high viscosity for increased stability. These high viscosity formulations need to be thoroughly mixed with the foaming water to be dispersed. It is very important that the antifoam is thoroughly dispersed for maximum cost-effectiveness. Otherwise, higher chemical dosages will be needed to reach the required surface or interfacial concentration.

Common antifoam application techniques are: spray directly onto the foam, drip onto the foam, drip into turbulence, or feed into a transfer pipe. The chosen method depends on physical layout and the characteristics of the antifoam formulation. An optimal application method involves applying antifoam chemical directly to the foam. To prevent foam, upstream chemical addition should be close to the foam-causing turbulence. Antifoam must be well mixed with the water to insure that the antifoam surfactants are dispersed and reach the air/water interface. Excess chemical discharge is the result of improper antifoam application and control.
This approach has minimal operator involvement, and antifoam is provided only when needed. The importance in wastewater applications is that only the minimal amount of chemical is used and discharged into the environment.

**CASE STUDIES**

Case I - An illustration of reduced antifoam usage is a surfactant plant in the southern United States. This particular facility produces surfactants used in household and industrial products. The foaming problem was erratic and unpredictable. Antifoam product was being supplied in drums, and plant operators needed to manually change drums. At times, the drum would run dry, and foam would become excessive, or the drums would be changed before they were empty. This led to increased disposal costs as well as wasted antifoam chemical. At this facility, antifoam usage was reduced by using a water-based product designed with a particular synergism which uses a combination of immiscible antifoam chemicals. As illustrated in Figure 4, equivalent foam control is obtained with twice the amount of a non synergism, silicon antifoam product, and 10X of a popular oil-based antifoam. By designing an antifoam without hazardous oils and using defoaming synergisms, chemical usage/pollution is minimized.

Additional chemical use was eliminated by examining the feed control system. An automated feed pump control system was installed, and a fouling-resistant probe was used to determine when excessive foam was occurring. With this system, antifoam chemical would be added only when foaming was detected. Another change was to supply chemical, in a tank, with a level gauge. This allowed operators to easily determine when the tank needed filling, eliminating erratic antifoam chemical supply as well as excessive drum disposal costs. These steps illustrate how utilizing synergisms, and automating feed systems prevents excess chemical discharge.

Case II - A surfactant facility in the Midwest illustrates the importance of antifoam application for pollution prevention. This facility produces the active ingredients found in many household detergents. Foaming was a problem, since excessive foam would spill over the aeration basin, onto a highway, creating a public hazard. This is illustrated in Figure 5. When antifoam chemical was added at the end of the aeration basin, there was little foam control, and high chemical dosages were needed. This particular antifoam chemical is not very water-soluble, and when added to water, an antifoam droplet settles to the bottom - it is not at the air/water interface. In this situation, the antifoam needed to be dispersed to control foam, by getting the defoaming chemical to the air/water interface. Adding chemical to the aerator turbulence disperses the antifoam, and acceptable foam control was possible using less antifoam chemical. Therefore, the application method can be very important in reducing chemical use/discharge.

**SUMMARY**

With increasingly stricter wastewater discharge regulations, the need to reduce pounds of hazardous chemical usage is more important. Wastewater antifoams can contribute to water
pollution and their composition/use needs to be examined. Fewer pounds of hydrocarbon oils are released into the environment when these oils are reduced or removed from the antifoam formulations. Defoaming synergisms can be used to minimize the antifoam chemical dosages needed for foam control. Also, utilizing antifoam synergisms reduces total antifoam pounds needed without degrading performance. This is especially beneficial when nonhazardous antifoam chemicals can work together to enhance defoaming. Finally, by controlling when and how much antifoam is used, the optimum dosage is delivered only when required. This reduces wasted antifoam product that would otherwise be discharged into the nation's waterways.


Lower surfactant concentration has a higher surface tension which is different from other regions of the same interface.

**Surface Tension Gradient**

**Bulk Viscous Flow**
(Lamella Drainage)

Figure 1 - The surface tension gradient opposes water flow from the lamella. Rate of lamella drainage is reduced and it takes longer for the bubbles to touch. This slows bubble coalescence.

**Lamellar Flow is Blocked**

**Oil Addition**
(micelles swell)

Figure 2 - Oil Swelling of Micelles Breaks up the Micelles Micro-structure.
Figure 3 - Synergism Mechanism

Reverse Maragoni Spreading drags the underlying liquid, pulling the interface down.

If Spreading Droplet is Associated with the second oil

$h3 < h2 < h1$ - Greater lamellar penetration depth at each stage. This reduces the time for complete lamellar bridging, increasing the bubble coalescence rate.

The Oils are not miscible. In an aqueous environment, one oil would associate with the other instead of with water, forming a large complex with greater penetration depth.
Figure 4 - Antifoam Usage Reduced Using Synergism.

Antifoam not dispersed when placed in non turbulent portion of basin.

Antifoam dispersed when added to aerator turbulence

Figure 5 - Antifoam Application can affect product performance. When antifoam product is added to a quiescent part of the aeration basin foam is not controlled. Changing the application point to mix antifoam