Technology Forum Article

Defoamer Selection in Waterborne Coatings

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Waterborne coatings systems differ from solventborne systems in a number of ways. One key difference is the fact that water displays a high surface tension, which must be lowered to allow spreading over low-energy substrates. But solving this problem often leads to another problem: the surfactants used to lower surface tension tend to stabilize foam. This foam, in turn, must be destabilized during manufacture and application through the use of a defoamer.

Choosing the proper defoamer for any given system has always been a matter of empirical selection. But today, new methods of analysis can help with that selection process. This article presents new and existing research in the areas of foam control and defoamer selection that can help minimize the amount of empirical work needed.

FOAM CONTROL

Foam problems in aqueous systems can arise during production as well as during application. Surface-active agents, such as emulsifying agents, wetting agents, and dispersants, are often formulated into coatings to achieve specific effects. These surfactants migrate to the coating's interfaces (gas/liquid, gas/solid, or liquid/solid) and usually lower the surface tension of the coating. However, an undesired side effect is the tendency of surfactant-bearing liquids to stabilize foam, once sufficient air is present.

Foam can be generated in a liquid with or without the presence of surfactants. Two kinds of foam may be produced: bubbles having a surface envelope when surfactants are present; or pure, uncoated air bubbles, in the case of a surfactant-free liquid. Air-containing bubbles tend to move upward to the surface of a liquid, where they behave differently depending on whether or not the liquid contains surfactant. Pure bubbles burst at the air interface, allowing the captured gas to escape and the liquid that was contained in the bubbles to flow together again. Bubbles that are covered by a surface envelope, by contrast, force the surfactant-layered liquid/air interface in front of them to the point of protruding through the surface, thus covering themselves with a double surfactant-lined envelope, called a lamella. This double layer of surfactant allows the formed structure to be stabilized.

The lamella-coated bubbles gather at the surface and form a foam-head, which consists initially of individual spheres, forced together in the most densely packed hexagonal array. By draining off liquid through the surfactant-rich lamellae, the spherical foam is transformed into polyhedral foam.

CAUSES OF FOAM

As described earlier, foam is created when air is introduced into the paint system, either during production or by the given method of application. Air can also be introduced into a paint through the chemical reaction of curing, as in the case of urethanes, or by application to porous substrates.

The prevention of bubbles is most difficult during application, as practically all of the captured air is transferred to the coating. Some methods employed to avoid this situation are film-casting and airless spray-painting, but even airless spray application can cause foam problems. Not only is air introduced into the system during stirring, but also during pressurization. As the coating is released from the orifice, it becomes further saturated with air from the atmosphere. Even more severe air entrapment occurs during air-assisted airless spray application. During drying, the air in the coating often cannot escape quickly enough, resulting in blisters and pinholes in the dried film.

DEFOAMER CHEMISTRY FOR AQUEOUS SYSTEMS

Typical defoamers include three key components: active substances, surface-active agents, and carrier fluids.

Active Substances

Active substances are those which prevent generation of foam, or break down the existing foam. The type of active substance to be used depends on the medium to be defoamed. The complexity of the paint system makes this task even more difficult than with single-component fluids. Selection is very important because the aesthetic look and the substrate-protecting attributes of the applied film should not be negatively influenced.

Traditionally, the largest classes of defoamers for aqueous systems are those based on petroleum hydrocarbon and/or silicone.

Aromatic and aliphatic petroleum derivatives traditionally have been used as active spreading substances in defoamer formulations. Aromatic oils were widely used in the past, but have come under fire recently for safety reasons. Aliphatic oils are less toxic, but their lack of compatibility in aqueous media

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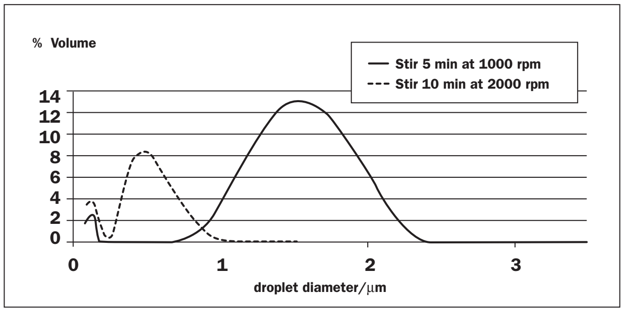
Figure 1

Droplet size distribution in the alkyd system using different incorporation methods

Defoamer: polyether siloxane (ethylene oxide/propylene oxide block-polyether) with polyether at the end of the polymer chain



causes serious gloss reduction in paints having moderate- to high-gloss. The relatively low hydrophobicity of mineral-oil based defoamers also means that higher dosages have to be used when compared to more hydrophobic materials. All active substances used in defoamer formulations conform to the following mechanisms: spreading by incompatibility and surfactant adsorption.

In many industrial applications, pure silicone oils are highly effective. However, their use in coatings often leads to severe surface defects, such as cratering and crawling. Much better compatibility can be obtained by modifying polysiloxanes with hydrophobic polyethers. This chemistry results in defoamers with very active spreading characteristics, combined with compatibility in many contemporary vehicle systems. What is more, this class of defoamers does not tend for have a negative effect on gloss or gloss definition.

This type of chemistry involves the synthesis of polysiloxane-polyether copolymers to contain either Si-O-C or Si-C linkages between the polyether and siloxane blocks. The siloxane block contributes surface activity, while the polyether block provides the degree of compatibility. A variety of structural possibilities exist, with the chemistry of the medium to be defoamed the determining factor.

Surface-Active Agents

Proper selection of the surface-active agent is critical to defoamer performance, and also influences the effect of the additive on surface defects. Surface-active agents focus defoamer activity at the air interface, bringing the active matter (e.g., hydrophobic silica) into contact with the stabilized foam structure. The surface-active agent must not be a foam stabilizer in its own right, as are some silicone-copolymers and fluorocarbons. Nor must the surface-active agent contribute to surfactant-induced defects such as craters and pinholes.

Carrier Fluids

Carrier fluids act to transfer the generally hydrophobic active substances uniformly into the hydrophilic medium. These fluids often have a lower surface tension than the medium to be defoamed, therefore actively helping to wet the lamella. Aliphatic and aromatic mineral oils, solvent blends, even water in the case of an oil/water emulsion, can be used as carrier fluids.

FACTORS THAT INFLUENCE DEFOAMER SELECTION

A defoamer must have a distinct degree of incompatibility with a given paint, otherwise it would not migrate to the air interface, and would not be available to break down stabilized foam. However, incompatible substances often cause surface defects such as fish-eyes, craters, and crawling. To minimize these negative side effects, defoamer formulations having a wide array of active ingredients and carrier fluids must be available to the formulator.

The selection of active compounds is determined by the anticipated application range. A mineral oil-based defoamer, for example, would be very suitable for flat to medium-gloss acrylic, styrene acrylic, and vinyl copolymer emulsions. But for medium- to high-gloss paints, the presence of mineral oil may cause loss of gloss definition. In general, the higher the gloss of the coating, the more critical defoamer selection becomes.

Hydrophobic polysiloxane-polyether copolymers are generally characterized by a high degree of incompatibility with the foaming medium (water/surfactant solution) while at the same time showing some compatibility with typical vehicles. This results in high defoaming activity while minimizing development of craters. Since polysiloxane-polyether copolymers defoam very well without hydrophobic solid matters, silica-free defoamers can be formulated that do not tend to affect the coating adversely.

Synthetic hydrophobic silicas have an essential impact on the efficiency of the defoamer. Defoaming silicas have specific surfaces ranging between 50 and 400 m^2/g. The average particle size should be between 0.01–1.0µ. The best defoaming is achieved if the hydrophobic silicic acid (silica/carrier fluid combination) approaches the viscosity of the liquid lamella.

The presence of hydrophobic matter in defoamers can cause various surface defects, particularly de-wetting flaws. Depending on the type of defoamer and the respective requirements, the amount of hydrophobic silicic acid should not exceed 15% of the final mixture. (For example, a flat or high pigment volume concentration [PVC] coating would show much less tendency toward surface defect formation than a lower PVC coating, allowing for a higher silica loading in the defoamer.)

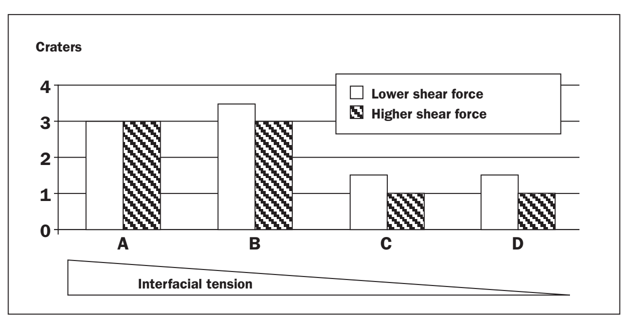
WHAT DETERMINES DEFOAMER EFFICIENCY?

According to the literature,[1-3] defoaming substances must be dispersed into fine droplets, allowing the active matter to get into the foam lamella and penetrate the surfactant film. At this point, a high spreading activity is essential for the defoamer. The resulting layer exhibits a drastic reduction in the structure's elasticity, which causes the lamella to burst.

Figure 2

Crater occurrence caused by different incorporation methods of active matter in the alkyd test system

(1 = no craters 4 = many craters)



All defoamers are polyether siloxane (ethylene oxide/propylene oxide block-polyether), with the following at the end of the polymer chain:

A. Polyether
B. Propylene oxide
C. More-hydrophilic polyether
D. Ethylene oxide

Incompatibility, high surface activity, and low surface tension are all necessary critical factors, but they are not the determining conditions for defoamer efficiency. More important are a positive entering (E) and spreading (S) coefficient[4,5] as defined in the following.

$$S = \gamma_m - \gamma_d - \gamma_{md} > 0$$
$$E = \gamma_m - \gamma_d + \gamma_{md} > 0$$

with γ_m as the surface tension of the medium, γ_d the surface tension of the defoamer droplets, and γ_{md} as the interfacial tension between the medium and the defoamer droplets.

The activity of defoaming substances can be strengthened through the incorporation of fine particles such as hydrophobic silica[6] or the in situ produced polyureas.[7] This process of foam destruction is called de-wetting. The surfactant film which stabilizes the foam lamella cannot wet the hydrophobic particles, so it pulls away.

Despite the many theoretical models for the function of defoamers, it is impossible to predict the ideal defoamer as an answer to a specific defoaming problem. Painstaking trial and error experiments can, in many cases, only be reduced by the formulation know-how of the paint producer and the raw material supplier. The wish for a highly active, compatible, easy to use, universal (including storage and shear stable) defoamer is far from attainable in practice. Because the request for the perfect defoamer narrows down to the determining parameters superior activity and minimum surface defects, a given defoamer is limited to a few systems, results are not transferable, and shear and storage stability in the formulation often will not be consistent.

DEFOAMER INCORPORATION

When using defoamers, it is readily observed that the foam-breaking activity, as well as the sensitivity to defects, depends on the manner in which the defoamer is incorporated.

Although defoamer oils are normally not soluble in paint systems, they are soluble as finely dispersed droplets throughout the matrix. The defoamer oil droplet size can be influenced by the intensity and time of shear forces. Higher shear force incorporation will result in finer droplet size (*Figure* 1).

Significant qualitative differences are found between moderate mixing speeds and actual grinding conditions. In the space between the glass beads, the defoamer droplets are subjected beyond laminar forces to severe turbulence, including pounding against the grinding vessel, becoming very effectively emulsified.

This situation confirms the groundwork published by Taylor,[8] Wu,[9] and Sundararaj,[10] whose work was concerned with the particle size distributions of finely dispersed phases in polymer matrixes. In general, the following inversely proportional equation between particle size (d) and shear rate (G) holds: [d = f (1/G)], where f is the sum of the constants of all components in a particular paint system.

TEST METHODS

Recent studies conducted by Tego Chemie Service, USA tested defoamer efficiency at 0.2% active matter on total formulation. Four types of defoamers were tested:

(1) a polyether siloxane (ethylene oxide/propylene oxide block-polyether) with propylene oxide at the end of the polymer chain;

(2) a polyether siloxane (ethylene oxide/propylene oxide block-polyether) with ethylene oxide at the end of the polymer chain;

(3) a polyether siloxane (ethylene oxide/propylene oxide block-polyether) with polyether at the end of the polymer chain; and

(4) a polyether siloxane (ethylene oxide/propylene oxide block-polyether) with a more-hydrophilic polyether at the end of the polymer chain.

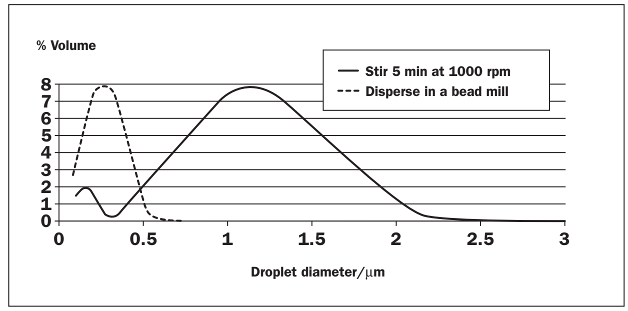
Each was added by stirring for one minute at 2,500 rpm. The amount of air entrapped was measured based on 45 gallons of paint.

All defoamers tested displayed fewer film defects in the paint when being incorporated with finer droplet sizes (*Figure* 2). However, the active matter retains its character of crater formation. Beside the attainment of a small droplet size, a more important factor in crater formation is the surface tension γ_{md} between the defoamer oil and the binder matrix.

Figure 3

Production of very fine droplets of the defoamer emulsion during the grind process

Defoamer: 20% emulsion of polyether siloxane (ethylene oxide/propylene oxide block-polyether) with propylene oxide at the end of the polymer chain



DEFOAMER EMULSIONS VERSUS COMPOUNDS

The addition of defoamer emulsions is preferred in situations where only mild stirring is possible, especially when sensitive binders are used, when adding to the let down, or when the defoamer is to be added to the finished paint. In emulsions, the defoamer droplets are already present in a finely dispersed form which can be easily incorporated into the paint. Defoamer emulsion addition to the grind operation can result in a dramatic loss of defoaming power, due to the reduction of the droplets to a size too small to be effective (*Figure* 3).

The emulsifiers in defoamer emulsions serve to degrade the interfacial tension γ_{md} and thus lead to finer droplet size. It holds overall that the defoamer droplet size is directly proportional to the interfacial tension between the defoamer droplet and the matrix [d = f (γ_{md})].

A fundamental result often repeated is that samples having a defoamer droplet size less than 1 µm have hardly any defoaming effect. Koczo, Lobo, and Wasan[11] as well as Prins[12] have suggested that drainage of the foam lamella, which is essential for foam breakdown,

Figure 4

Droplet size distribution after grinding in a mill base

Defoamer: polyether siloxane (ethylene oxide/propylene oxide block-polyether) with propylene oxide at the end of the polymer chain

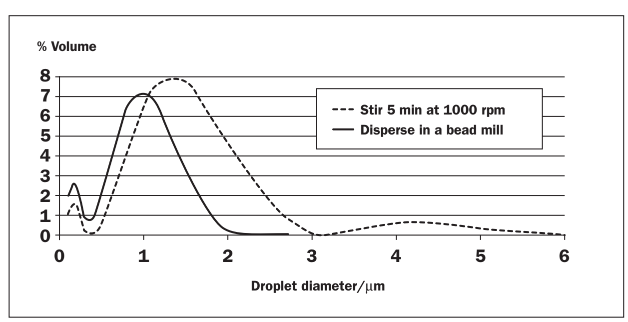
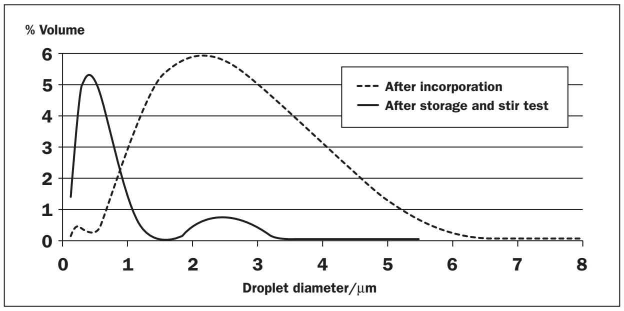


Figure 5

Typical defoamer droplet size distribution – initial and after storage & stir test

3 weeks storage at room temperature



is sufficiently hindered if the diameter of the droplets is less than 1 µm.

To reduce foam formation during the grinding process, 100% active matter defoamers, or "compounds," are better employed because they can withstand high shear forces (*Figure* 4). This holds especially when the viscosity ratio between the droplets (η_d) and the matrix (η_m) is large.

Higher-speed shear for a longer period of time (G), lower interfacial tension (γ_{md}) between defoamer oil and binder matrix, lower viscosity of the defoamer droplet (η_d) and higher viscosity of the system to be defoamed (η_m) determine the droplet size (d) of the defoamer oil, as described in the following formula:

$$d = f\,(\gamma_{md}\ \eta_d \ / \ G\ \eta_m)$$

DEFOAMER PERSISTENCE AND STORAGE STABILITY

The parameters during incorporation determine the character of the system shortly after production. The performance after storage might be totally different. The choice of the right defoamer is especially difficult for waterborne systems because many products show good performance after production and lose efficiency with time.

Many defoamers show only a little change in the curve on droplet size measurement after storage. On short exposure to shear (as by the stir test and naturally by different application methods), however, dramatic change toward very fine distribution of the polyether siloxane droplets occurs due to better dispersion of the active matter (*Figure* 5). This is caused by surface active substances in the system which, during storage, merge to the droplet surface and reduce the interfacial tension between the active matter and the matrix, resulting in a loss of defoamer efficiency.

To achieve the greatest efficiency of the defoamer on storage, it is recommended to use products with high interfacial tension (γ_{md}).

CONCLUSIONS

In practice, defoaming activity is a complicated process involving defoamer droplet size and interfacial tension.

For the defoamer supplier and the formulator, the discussed physical relationship suggests the recommendation of defoamer compounds for use where defoamers can be incorporated with high to medium shear; defoamer emulsions are for applications having minimal shear requirements, including post-addition, to maintain their predetermined optimized particle size distribution. Alternatively modern compounds having lower interfacial tension can be recommended.

The defoamer droplet size distributions obtained by different methods of incorporation determine the character of the coating system shortly after production. Defoamer oils with low interfacial tension, in particular, show loss of efficiency after storage due to finer droplet sizes after exposure to new shear forces. Defoamer oils with high interfacial tensions promise better stability; on the other hand, low interfacial tensions lead to fewer surface defects.

For high performance, defoamer droplet sizes between 2-10 µm are ideal. The suitable active matter depends on the emulsifying character of the binder system. By the variation of polyether siloxane structure, defoamers can be customized for specific coatings.

Even though all of the various relationships are not completely understood yet, enough data exists to limit the amount of empirical work necessary for defoamer development.

References

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