Foam Control in Aqueous Coatings

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Causes of foam
Foam is a stable dispersion of a gas in a liquid medium that results when a surfactant layer forms around air bubbles and entrains them within it. Air can be incorporated into a coating by mixing during the polymer/pigment grinding and let-down steps, by pumping during package filling or by shear or spraying during application. Effective foam control agents are beneficial in preventing or reducing many common coating problems such as:

• Viscosity increase and loss of mechanical shearing power during milling (resulting in smaller batch sizes and poor pigment/polymer dispersion).
• Volume increase during the let-down and mixing steps leading to overflowing.
• Slower package filling rates due to inefficient pumping.
• Air incorporation during transport and handling.
• Slower printing press speeds or lower pressures during spraying.
• Surface defects on coated substrates resulting in poor appearance, reduction in gloss or less substrate protection.

Stable foams occur when surfactants are present, forming an interfacial layer around air bubbles that are entrained in the coating medium. Unfortunately, surfactants are essential components of water-based formulations since they function as emulsifying agents for the polymeric binders, as dispersing agents for the pigments and fillers and as wetting agents to modify the spreading characteristics of the coating. Also, the dispersing and mixing stages during manufacture cause entrapment of air. If the physical and chemical conditions that cause foam cannot be altered, the addition of a foam-preventing or -destroying agent is the best option available to the formulator.

Foam destabilization mechanisms
Foam control agents can be classified as antifoams or defoamers. Although the two terms are often used interchangeably, strictly speaking, antifoams prevent the formation of stable foams, while defoamers act by destabilizing already existing foams. Foam control agents function by a variety of mechanisms to prevent or rupture foam. Individual antifoam efficiency is determined by three key factors:

• Insolubility of the antifoam agent in the foaming medium
• Low surface tension, so that it can be uniformly dispersed through the formulation
• Ability to penetrate into the foam wall (or lamellae)

Foam control agents or defoamers must be insoluble in the foaming medium. They function by being more surface active than the surfactant stabilizing the foam so that they are able to enter the surface layers of the potentially foaming liquid and displace it from the gas/liquid interface. The mixed surfactant layers now prevent close association of molecules and exhibit low elasticity. The presence of random, highly surface active, insoluble molecules in the surface film interrupts foam stabilization via the Marangoni effect and thus foaming is prevented.

The four basic processes by which antifoams disrupt aqueous foam are: entering, bridging, de-wetting and rupture as depicted in Figure 1. This mechanism proposes that droplets of the antifoam move to the foam lamellae where they provide a point source for rupture of first one air/water interface and then the other. An oil lens is then formed, which bridges the air-water-air foam film. Drainage in the oil lens and foam film takes place until eventually the film ruptures. The thermodynamic factors and surface properties influencing the foam control mechanism and foam stability have been discussed in the literature. Higher bulk viscosity systems, such as formulations containing thickeners or high binder content, slow down the displacement of the liquid from the lamella and limit the mobility of the entrained air bubbles. Surfactants orient at the air-liquid interface to create a higher surface viscosity in the lamella than the bulk in which film drainage can be impeded. The surfactant stabilizes foam by hydrogen bonding and electrostatic repulsion between surfactant molecules within the lamella. Increased surface elasticity created by the thinning of the lamellae also impedes liquid drainage.
and subsequent foam collapse. Movement of the surfactant layer can actually pump water back into the lamella causing further stabilization (Maragoni effect).

Why use silicones?
The term silicone refers to a class of materials characterized by an Si-O-Si backbone. The simplest polymer, sometimes referred to as silicone oil, is polydimethylsiloxane (PDMS).

\[(\text{CH}_3)_3\text{SiO-(Si(CH}_3)_2\text{O)}_n\text{Si(CH}_3)_3\]

where \(n = 0\) to \(>1000\).

Two properties of silicones make them suitable as aqueous foam control agents; they are very hydrophobic and therefore incompatible with water, and they are also highly surface active with liquid surface tension values of approximately 20 mN/m. Both these properties ensure that silicones will migrate to the air/liquid interface of bubbles within a coating.

Types of silicone-based defoamers
The simplest silicone-based system is PDMS alone. It is known that PDMS will migrate to the surface of a film and remain there. If the surface consists of macro-bubbles, it may penetrate and spread over the foam lamellae, but its ability to destroy foam is limited. The main disadvantage is that PDMS is so insoluble that it is very difficult to disperse in water-based systems and almost inevitably causes surface defects. Polydimethylsiloxanes are typically emulsified when added to aqueous coating systems using organic or silicone-based surfactants to assist in delivering the foam control active and to help with leveling/wetting of the applied coating. In addition, a hydrophobic particle may be incorporated into the fluid, then used as a compound or emulsified to assist with antifoam entry and subsequent foam rupture. Blends of PDMS and silica are often referred to as silicone compounds. Experience has shown that they can cause problems; they are extremely incompatible with the foaming medium, which makes them difficult to disperse, but they are also incompatible with the resin binders leading to dewetting of the coating as it dries and leaving defects in the dried films often described as fisheyes, cissing, etc.

So the problem of dispersion has been resolved, but the problems caused by the incompatibility of PDMS in the drying film still need to be addressed. This has been done by incorporating modified PDMS in the form of silicone-polyether copolymers into the foam control formulations. The copolymers are synthesized from reactive siloxanes and polyethylene/polypropylene glycol ethers. A range of structures is available, for example branched, block or pendant copolymers. Figure 2 illustrates both the rake structure where the polyether groups are pendant to the siloxane backbone and the ABA structure where the polyether groups end-cap the siloxane polymer. By varying the hydrophilic/hydrophobic nature of the silicone polyether, these materials can be used in conjunction with PDMS fluids and compounds as emulsifiers and wetting agent components of an antifoam compound or emulsion. Silicone polyethers have also been formulated with glycols to form easily incorporated dispersions for applications such as architectural paints but they can also be designed to function as effective antifoams alone. Potential benefits for polymeric silicone polyether used as the sole antifoam in a coating or ink include:

- 100% active to allow greater formulation flexibility and lower use levels.
- Self-emulsifying for easier incorporation into aqueous or polar coatings.

Figure 2: General structure of a rake and ABA silicone polyether

\[
\text{(CH)}_3\text{Si} \quad \text{i} \quad \text{i} \quad \text{i} \quad \text{i} \quad \text{i}
\]

Rake or pendant

\[
\text{(EO)} \quad - \quad -
\]

ABA or linear

where \(R\) = OH, OR, acetate

Figure 3: The defoamer performance balance
Conclusions
Silicone-based antifoams have progressed markedly since the first use of PDMS fluids in solvent-borne coatings and inks. Keeping pace with formulation changes and environmental drivers, silicone antifoams have evolved to comprise a variety of delivery systems and polymer types to meet the specific requirements of diverse formulations. For waterborne coatings and inks, the product offerings have been expanded to include novel silicone polyether-based antifoams that offer effective foam control balanced against ease of incorporation and good coated surface appearance.

As coating formulators are aware, no "universal" foam control agent has been developed to date. Therefore, any foam control agent should be evaluated in a particular formulation for suitability.

For information about specific product options, consult the Dow Corning® Silicone Foam Control Agents for Waterborne Coatings selection guide.

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