

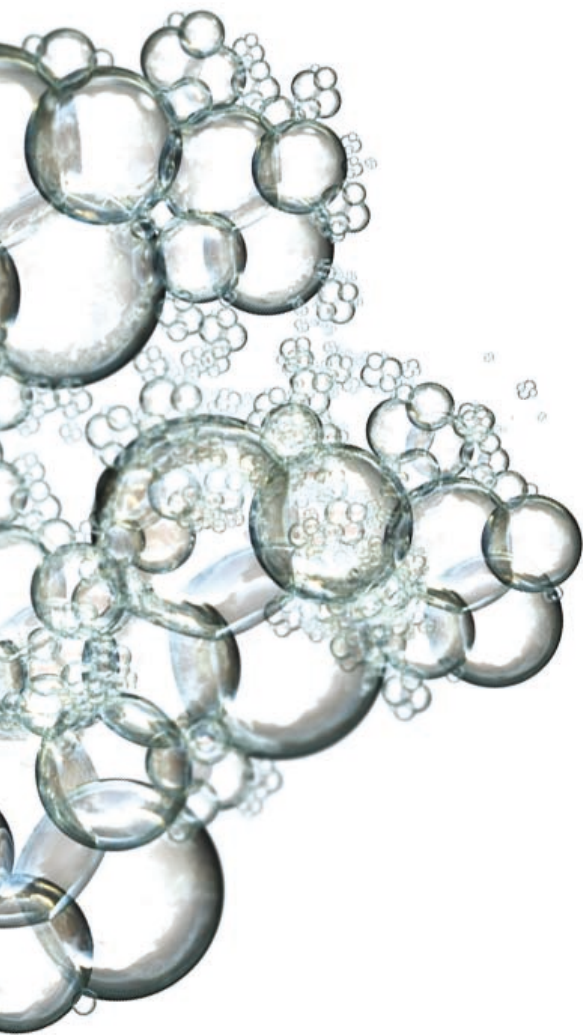
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Technical Information L-DI 1

# Defoamers and Air Release Additives

# Defoamers and Air Release Additives



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## What is Foam?

Foam is always undesirable in coatings. Foam formed during the paint production process, leads to non-optimal fill of the production vessels and causes problems in the filling line. Additionally, – and here is where most of the problems arise – foam can also occur during application, thus causing surface defects. Foam in the coatings film is not only an optical disturbance, but also reduces the protective function of the coating. Accordingly, a defoamer is an essential ingredient in nearly all coating formulations.

Many components of a coating system can affect its foaming behavior, either positively or negatively. Additionally, the characteristics of the substrate and application parameters also have an influence. One must realize that foam is very much "situation specific." For instance, a particular spray application may result in excellent film properties; nevertheless, application of the exact same paint system on a curtain coater will exhibit foaming problems. Since we are restricting our observations to coatings systems, only fluid foams will be discussed. Such foams are defined as a fine distribution of a gas (normally air) in a liquid phase. A characteristic feature of foam (as compared to other physical states) is the extremely large interface between the gas and the liquid. The liquid layer surrounding the air volume separating the gas bubbles from one another is called the lamella. For energy reasons, every liquid system attempts to keep its surface area as small as possible. Since foam represents a high-energy state, it can only exist because of foam-stabilizing effects.

Immediately after formation, the gas bubbles rise through the liquid to reach the surface. According to Stokes' Law, the rate of rise ( $V$ ) is dependent upon the radius ( $r$ ) of the bubbles and the viscosity ( $\eta$ ) of the liquid.

$$V \sim \frac{r^2}{\eta}$$

When a typical gas bubble reaches the surface, liquid starts to flow from the foam lamella (the thin liquid film surrounding the gas bubble). This flow process (drainage effect, figure 1) reduces the thickness of the lamella and when the thickness is less than approx. 10 nm, the lamella loses its integrity and the foam bubble breaks.

If the behavior of all liquids were to precisely follow the above pattern, then there would be no foaming problems since stable foam bubbles could not form. This is the case, for example, with pure liquids; pure liquids do not foam. In order to form stable foam bubbles, foam-stabilizing substances must be present in the liquid phase.

In general, such substances are interfacially active materials (surfactants, tensides, etc.) that are characterized by the presence of hydrophobic and hydrophilic segments within their molecular structures. Because of these structural elements, such substances orient themselves at liquid/gas interfaces to reduce interfacial tensions, thus producing the necessary conditions for foam stabilization (figure 2). ➤

### Drainage Effect

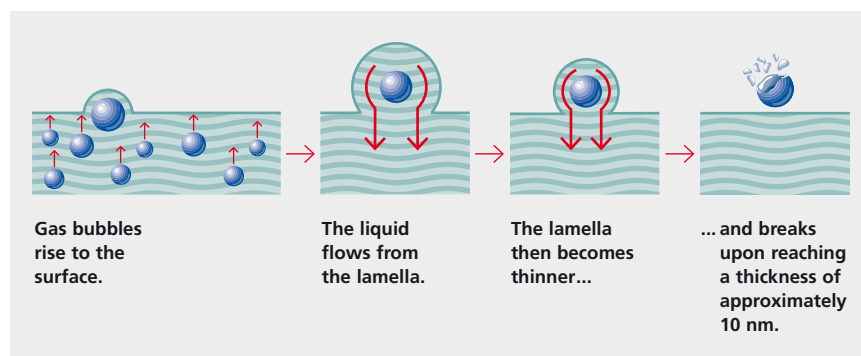


figure 1

### Foam Stabilization through Surfactants

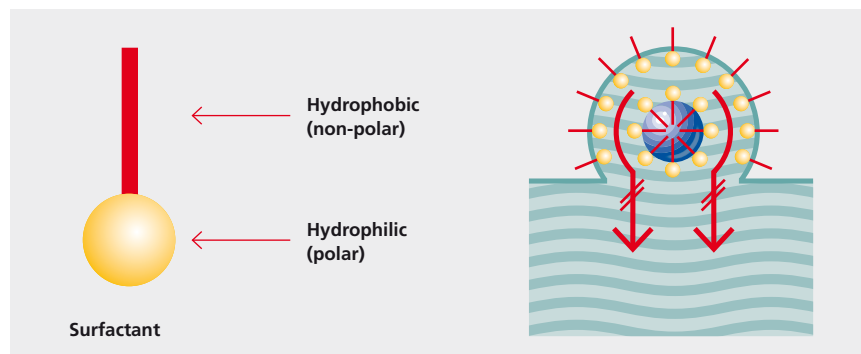


figure 2

## › What is Foam?

Every paint formulation (aqueous, solvent-free, or solvent-borne) contains a multitude of foam-stabilizing ingredients of varying origins and chemical structures. Consequently, every formulation, in principle, can exhibit foaming. As one follows a typical foam's "life history," so to speak, the observer can see that the structure of given foam changes over time. Immediately after formation, foam bubbles contain an abundance of liquid (figure 3); this structure is called "wet foam" or "spherical foam" because the bubbles are spherically shaped and do not, to any appreciable extent, deform each other.

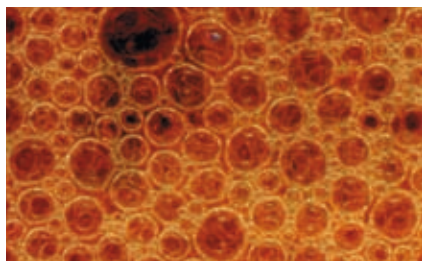
As described earlier, liquid then flows from the foam lamellae (drainage effect); the lamellae become thinner; the gas bubbles pack together more densely to form polyhedral structures. The resultant

foam structure is called "dry" or "polyhedral" foam. In the absence of opposing forces, the described drainage effect would eventually thin the lamella walls to the point where the foam would simply collapse.

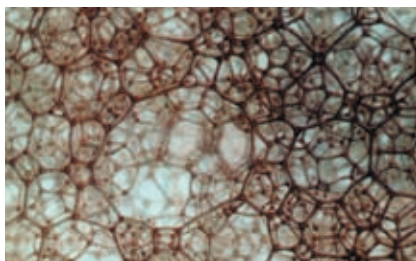
One important opposing force occurs as a result of the chemical structure of the foam stabilizing ingredients (surfactants). In water-borne or aqueous systems, the hydrophilic groups are ionic in nature. The two surfactant-laden interfaces of a foam lamella come closer together as liquid drains. When they are close enough, repulsive forces eventually begin to take effect; namely, like-charged electrical entities repel one another. Therefore, further drainage of the lamella, and break-up of the foam are hindered by the electrostatic repulsion of the surfactant molecules (figure 4).

A further stabilizing effect is the elasticity of the foam lamella (figure 5). When the lamella is stretched, this stretching action itself causes a reduction of the surfactant concentration at the interface (since the volume of liquid now has a larger surface area to which the surface molecules must orient). However, lowering the surfactant concentration at the surface increases surface tension, which, in turn, pulls the lamella back together. This particular foamstabilizing effect is called Gibbs elasticity. There are other additional effects that are interesting in the context of studying foam behavior; however, additional theoretical background effects will not be discussed further.

### Structure of Foam



Spherical foam



Polyhedral foam

figure 3

### Foam Stabilization through electrostatic Repulsion

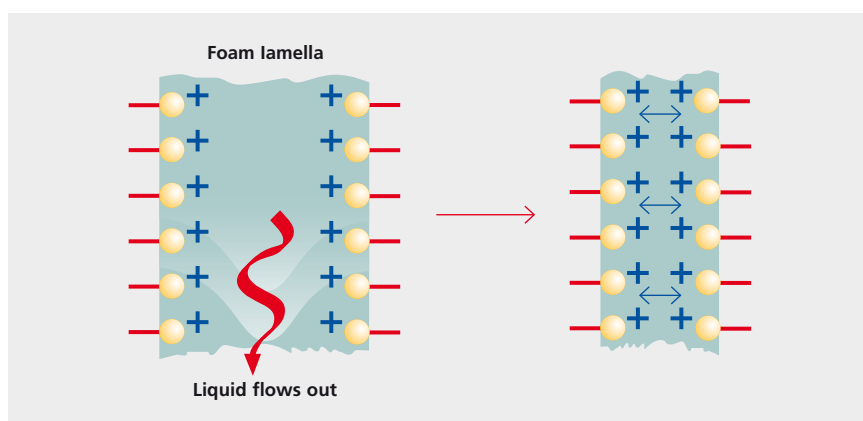


figure 4

### Foam Stabilization through Gibbs Elasticity

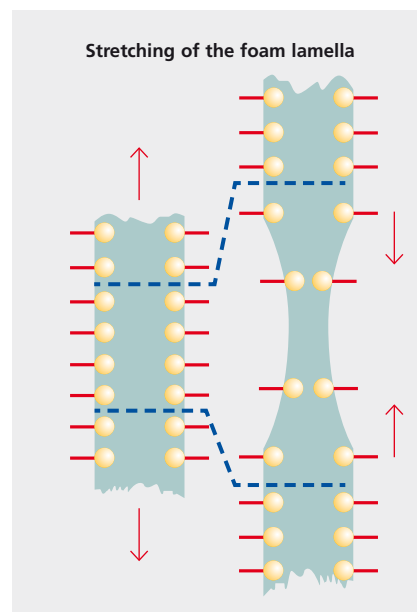


figure 5

## The Modes of Action of Defoamers and Air Release Additives

Since it is virtually impossible to escape the presence of foam stabilizing substances in coating systems, defoamers are employed to avoid the formation of foam and/or to destroy (as rapidly as possible) existing foam.

Defoamers are low surface tension liquids which, generally, must demonstrate the following three properties:

- Insolubility in the medium to be defoamed
- Positive entering coefficient
- Positive spreading coefficient

When the entering coefficient is positive, the defoamer will be able to enter the foam lamella. If, in addition, the spreading coefficient is positive, then the defoamer will spread within the interface (figure 6). Because of this spreading effect, the foam stabilizing surfactants are displaced, and the previously elastic, disturbance-resisting lamella is turned into a film with reduced cohesive forces.

The defoaming efficiency of such defoamer liquids can be accentuated (especially in aqueous systems) by the addition of finely dispersed hydrophobic particles (e.g. hydrophobic silica or polyurea). The defoamer liquid serves as a carrier medium that transports the particles into the foam lamella. These hydrophobic particles behave as "foreign" particles in the hydrophilic liquid lamella and contribute to foam destabilization through the reduction of cohesive forces. Additionally, such particles adsorb or "capture" surfactant molecules (surfactant scavengers), thereby causing the foam lamella to collapse (figure 7). ➤

### Defoamer enters the Foam Lamella

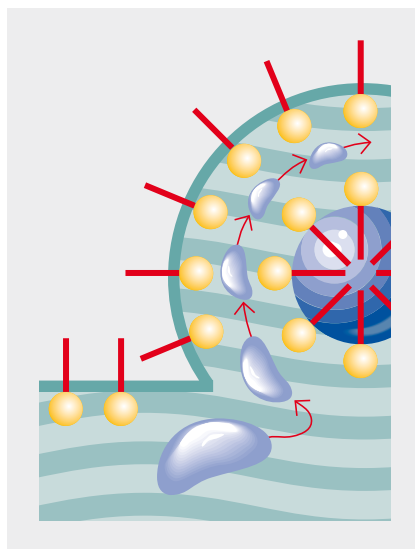


figure 6

### Defoaming through Hydrophobic Particles

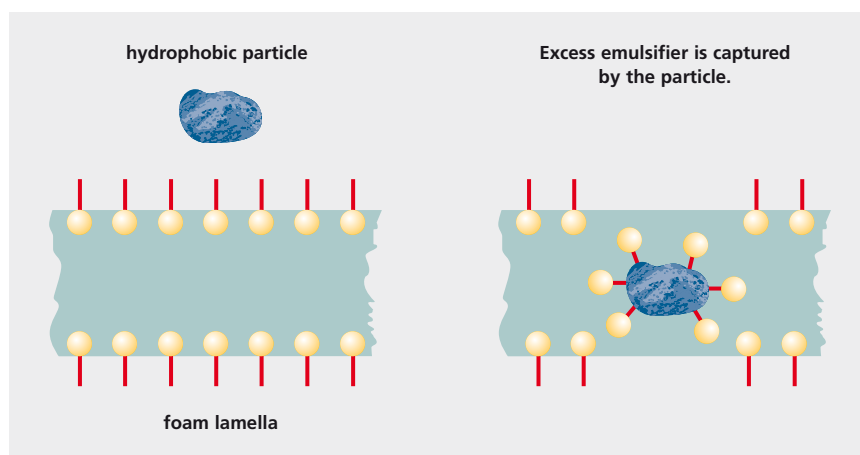


figure 7

## > The Modes of Action of Defoamers and Air Release Additives

Another important property of all defoamers is their “selective (or controlled) incompatibility” with the medium to be defoamed. A defoamer that is too compatible will not migrate into the foam lamella, but rather into the bulk of the coating system. In this case, the defoaming properties are minimal. Defoamers that are too incompatible, on the other hand, may lead to paint defects such as haze or craters. The selection of the proper defoamer can be characterized as a “balancing act” between compatibility and incompatibility. In figure 8, this correlation is illustrated: too much compatibility can lead to foamstabilization instead of defoaming. Of course, the optimum exists, when proper defoaming without defects (haze, craters) is achieved.

Due to the wide variety of paint systems, one defoamer cannot be optimal for all formulations. A range of various defoamer products is necessary in order to offer a suitable product for each purpose. The fine-tuning of the defoaming action can be achieved by varying the dosage: more defoamer in general, brings better defoaming. However, it may increase defects or make them visible. Reducing the dosage avoids film defects but the defoaming action may not be sufficient.

The term “defoaming” is often used to describe the removal of gas bubbles from coatings. At times, however, it is useful to differentiate between “defoaming” and “air release” (figure 9). First, the gas bubbles have to get to the surface; this step is called air release. The subsequent destruction of the foam bubbles at the surface is referred to as defoaming. Air release additives function to increase the rising speed of the bubbles. These additives help to coalesce adjacent small foam bubbles within the coating to bigger bubbles, which, due to their increased size, move more rapidly to the surface (Stokes’ Law). Air release additives must be active throughout the entire paint film for this to occur. Conversely, defoamers are only active at the surface, where they destroy the surface air bubbles.

In practice, however, it is not always possible to distinguish between these two effects and to define the effectiveness of an additive solely as a defoamer or an air release additive. Consequently, subsequent discussion will generally employ the term “defoamer”, even when in isolated instances, the term “air release agent” might be somewhat more appropriate. The following discussion will focus upon the chemistry of BYK-produced defoamers for aqueous and solvent-borne systems, that can be categorized into the following groups:

- Mineral oil defoamers
- Silicone defoamers
- Silicone-free polymeric defoamers

### Optimal Defoaming Behavior

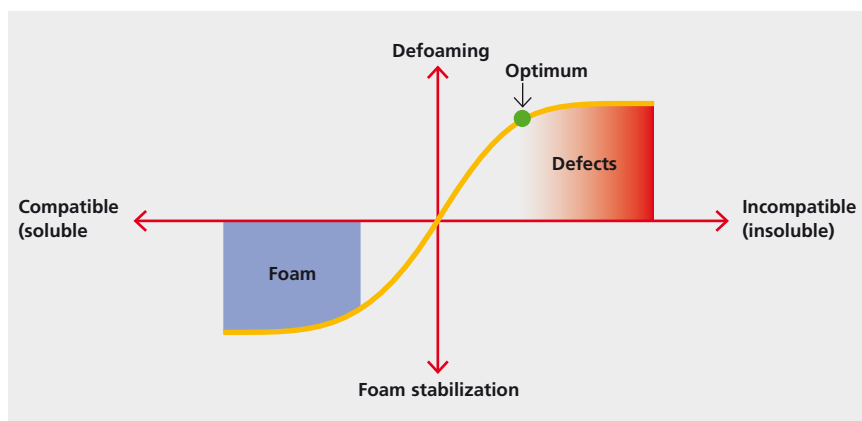
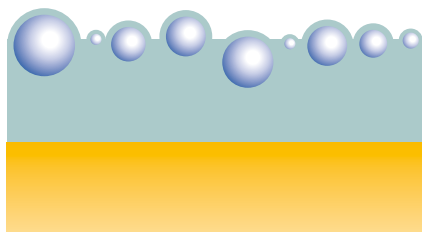
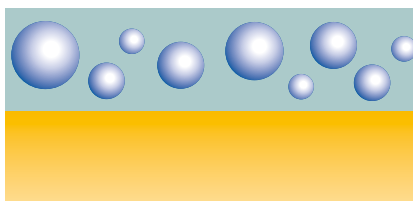


figure 8

### Defoaming and Air Release



Foam on the surface. Defoamers destabilize the foam bubbles.



Air incorporation within the paint film itself. Air release additives accelerate the migration of the bubbles to the surface.

figure 9



## Mineral Oil Defoamers

The BYK-030-Family represents the BYK mineral oil type defoamers. Generally, mineral oil defoamers are intended primarily for flat and semigloss emulsion paints and emulsion plasters. In higher quality aqueous industrial coatings, mineral oil defoamers are not suitable as they can cause surface defects (oil separation, gloss reduction). Additionally, in solvent-borne systems they should not be used, because their spreading efficiency is not sufficient.

A mineral oil defoamer consists of approximately 85% carrier oil and 10% hydrophobic particles. The remaining 5% are emulsifiers, biocides and other performance enhancing ingredients. As the carrier oil, aromatic or aliphatic mineral oils can be considered. Aromatic products are no longer employed by BYK since they may cause premature yellowing and present physiological handling risks due to their high levels of polycyclic aromatic hydrocarbons. Hydrophobic particles also exhibit a decisive influence upon defoamer behavior. Hydrophobic fumed silicas are typically employed. However, in this respect, BYK defoamers greatly differentiate themselves from traditional defoamers because they are based upon patented technology that uses polyurea compounds as hydrophobic particles. In addition to demonstrating increased defoaming action, these patented compounds exhibit two additional advantages:

1. The polyurea is synthesized from liquid reactants in situ in the carrier oil, thus leading to a much finer size particles and improved settling resistance. The defoamer itself exhibits better storage stability.
2. Because of larger specific surface area, the adsorption capacity for surfactants is greater. This in turn assures optimal defoaming activity, even after longterm storage of the coating.

The emulsifiers utilized in defoamers are required to disperse the particles within the carrier oil. In addition, they facilitate the incorporation of the defoamer into the paint formulation.

Alkyl phenol ethoxylates are often used as emulsifiers. If due to health considerations, this type of emulsifier type is not permitted, defoamers with compliant (APE-free) emulsifiers are available.

Especially high quality defoamers for high gloss emulsions, often contain small amounts of a modified polysiloxane in order to increase spontaneous defoaming action.



## Silicone Defoamers

Silicone defoamers are liquids with exceptionally low surface tension containing polysiloxanes as the main active ingredients. The chemical structure of the polysiloxane is the deciding factor in determining defoaming efficiency. For example, the relatively shortchain polysiloxanes (which are used as surface additives, see Technical Information L-SI 1) can demonstrate foam stabilizing, rather than foam destabilizing (defoaming)

behavior. Whether or not a particular polysiloxane functions as a foam stabilizer or a defoamer depends upon its compatibility and solubility in the liquid medium at hand; only incompatible and insoluble polysiloxanes function as defoamers.

Figure 10 illustrates this point in regard to pure (unmodified) dimethylpolysiloxanes. The controlling factor here is the molecular weight or chain length of the silicone. Lower molecular weight products function as foam stabilizers; higher molecular weight analogs are sufficiently incompatible to show defoaming effects; and finally, the highest molecular weight products (hammer finish silicones) are completely incompatible.

The required "selective incompatibility" can be achieved through a variety of silicone chemistry techniques.

By modifying the silicone backbone with various organic side chains, compatibility can be controlled. The introduction of polyether chains ( $R^1$  in figure 11) based on ethylene oxide increases hydrophilicity and, therefore, as a rule, increases compatibility in polar systems.

Polyethers based on propylene oxide result in more hydrophobic structures. In place of the dimethyl polysiloxanes, methylalkyl polysiloxanes can be employed. The exchange of the second methyl group with a longer alkyl chain ( $R^2$  in figure 11) leads to higher surface tension values of the polysiloxane. In general, this means a decrease in foam stabilization behavior.

Recent innovations include the availability of defoamers with perfluorinated organic modifications, the so called "fluorosilicone defoamers". These products distinguish themselves by their very low surface tensions and their strong defoaming behavior.

### Dimethylpolysiloxanes

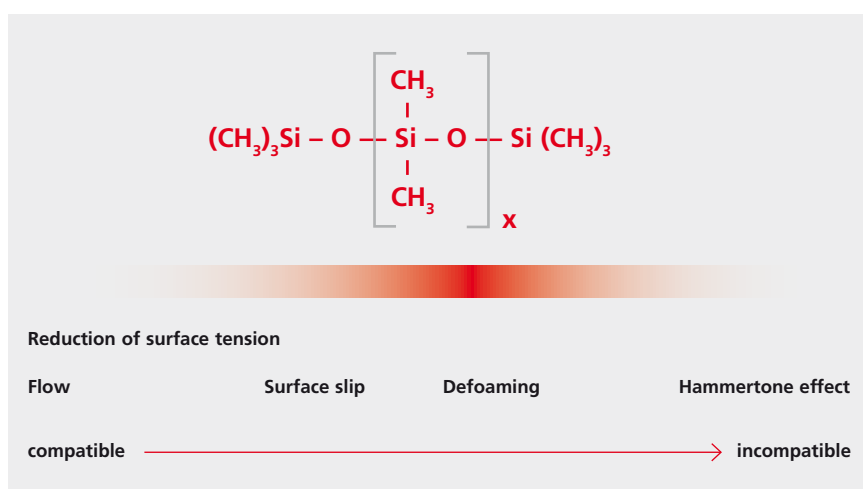


figure 10

### Organically modified Polysiloxanes

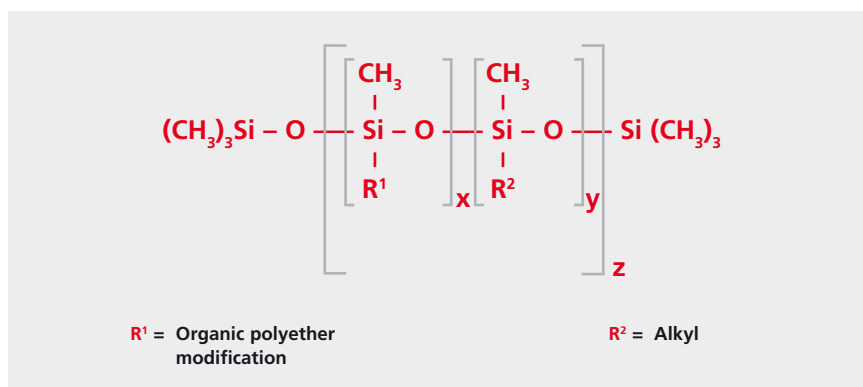


figure 11



### Silicone Defoamers for Aqueous Coatings

Silicone defoamers for aqueous systems are mostly emulsions of highly hydrophobic silicone oils. Due to their silicone content, they are more expensive than mineral oil defoamers and therefore designed for use in high quality coatings formulations. Silicone defoamers also make use of hydrophobic particles (polyureas) in order to improve dispersibility and defoaming performance. The primary advantage of silicone defoamers (as compared to mineral oil defoamers) is that they neither reduce gloss in high gloss systems, nor do they reduce color acceptance when used with pigment concentrates.

To achieve craterfree coatings, sufficiently high shear forces must be used during incorporation of the defoamers.

Highly incompatible defoamers must be added to the millbase. When less incompatible defoamers are employed, e.g. the standard defoamer BYK-028, the shear forces available for the letdown stage are sufficient. A very compatible defoamer such as BYK-025, is extremely easy to incorporate and can be post-added to a curtain coater without disrupting the curtain. Low priced silicone defoamers, BYK-045, BYK-1610 and BYK-1615 have been developed specifically for decorative emulsion paints. BYK-1610 and BYK-1615 can replace the mineral oil defoamers which are typically used in emulsion paints and emulsion plasters.

### Silicone Defoamers for Solvent-based Systems

BYK-065 and BYK-066N are two fluoro modified polysiloxanes with broad applications. They offer highly efficient defoaming even with minimal amounts of incompatible ingredients. BYK-070, BYK-088 and BYK-141 are somewhat more compatible; the active substance of BYK-088 is FDA §175.300 compliant and is designed especially for aromaticfree formulations.

Apart from the actual "silicone defoamers," there also exists a special group of silicone surface additives that exhibit defoaming properties. The particular products of interest are always methylalkyl polysiloxanes. Such products should be utilized when the foam problem is not too severe and typical silicone properties are also required (such as increased slip and the prevention of Bénard cells). Obviously, whenever the defoamer properties of the aforementioned products are not sufficient, then combinations with silicone defoamers or silicone-free polymeric defoamers would be appropriate.



## Silicone-free Polymeric Defoamers

In addition to polysiloxanes, other polymeric products can defoam through their selective incompatibility. The proper balance between "compatibility" and "incompatibility" can be achieved by modifying the polarity and the molecular weight (molecular weight distribution) of the polymers.

Unfortunately, there is no published data to correlate defoamer behavior and the chemistry of the special polymeric defoamer compounds.

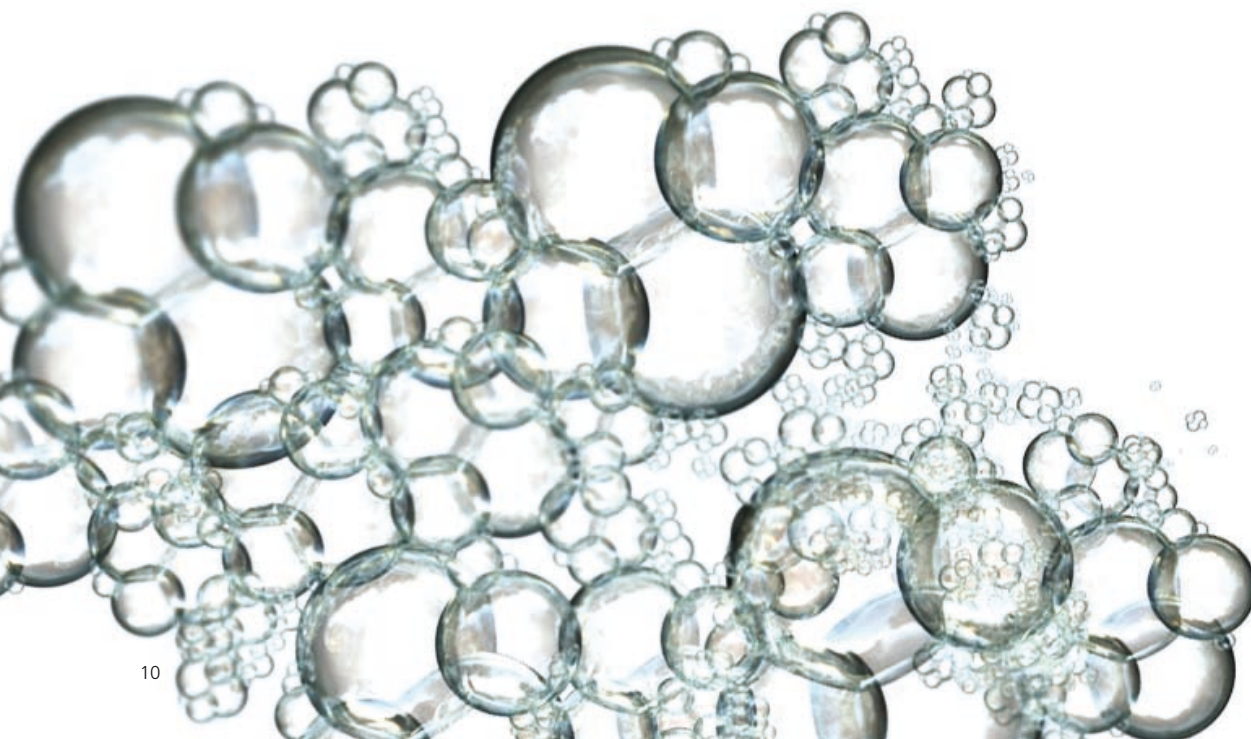
With regard to silicone-free defoamers for solvent-borne systems, BYK-052 is the standard product. BYK-051, BYK-052, and BYK-053 form an integrated product family based on the same chemistry with different molecular weights, thus different degrees of incompatibility. The lowest molecular weight product, BYK-051, is obviously the most compatible while the highest molecular weight product, BYK-053 is the least compatible.

BYK-1752 is a version of BYK-052 without aromatic solvents.

BYK-011 and BYK-012 are silicone free polymeric defoamers for high quality, aqueous coatings.

At this point, it is also useful to mention BYK-354, BYK-355, BYK-361, and BYK-390. These products are primarily acrylic leveling additives but often also function as defoamers or air release additives in many systems.

BYK-390 and BYK-392 are recommended for preventing boiling marks (solvent pops), in baking systems.



## Selection Criteria and Test Methods

Since defoaming action itself is the most important selection criterion for defoamers, many different test methods are employed.

In order to distinguish performance between the control (no additive) and the various samples with defoamers, a reproducible method of incorporating air (or producing foam) must be employed. The main point is the production of as much or as little foam as necessary to differentiate the test results. "Absolute" methods are not required, since the results are always compared to the control.

Possible ways to create foam are: shaking the paint in a graduated cylinder, moving a disk with holes up and down in the paint or blowing air into the system through a piece of porous glass or ceramic. The volume of the foam created can then be measured (figure 12). Another standard method uses a high speed dissolver to stir in air under controlled conditions (time and speed). Afterwards, the foamed paint is poured onto a tilted glass panel. While the paint is flowing down, breaking of the bubbles can be observed and after drying, the number of the remaining bubbles can be used to evaluate defoaming efficiency. When the glass panel is lit from behind, even the smallest bubbles become visible. The methods described ignore completely the way the paint will be applied in practice. But more application-related test methods are also available: Emulsion paints can be evaluated by application with a foam roller; to intensify foam formation, a roller with extremely large pores is used (figure 13). Testing of decorative architectural coatings can be conducted using brush application; the brush is handled in such a manner as to create as much foam as possible (figure 14). In highly filled systems (such as plasters), density measurements are most useful; the highest density sample exhibits the best foam removal.

When dealing with aqueous emulsions, often the foaming tendency of the pure (diluted) emulsion is evaluated. This is very quick and easy but should be viewed only as a pretest. The final coating formulation contains numerous additional components that can also influence foaming behavior and it is therefore mandatory that defoamer tests be conducted in the final coating system itself. The coating should be tested approximately 24 hours after defoamer incorporation. In addition, evaluations after storage are necessary, since defoamers can lose effectiveness over time. Significant performance differences can be noted after only four weeks storage at 50 °C/122 °F.

Combinations of a defoamer with an (acrylic) leveling additive can be beneficial: after the breaking of foam bubbles, the coating surface can level out quickly and the formation of pinholes and dimples is avoided. Defoamers are effective when they are insoluble in the medium to be defoamed and when they display a certain degree of selective (controlled) incompatibility. Due to this incompatibility, the following potential side effects can occur:

- Gloss reduction
- Turbidity (in clears)
- Craters

Depending on the details of the paint formulations, individual defoamer products behave differently in regard to these potential side effects, they must not be neglected when making defoamer selections. Tests at various defoamer levels are obviously recommended, so that the proper balance between the desired defoaming action and the undesirable side effects can be reached. Whether or not a particular coating system exhibits foam problems is dependent not only upon the formulation itself, but also upon substrate conditions and application parameters. One should always attempt to include the most important parameters into the evaluation procedure. Such inclusion provides the only guarantee of obtaining both definitive and practical results.

### Measurement of Foam Volume

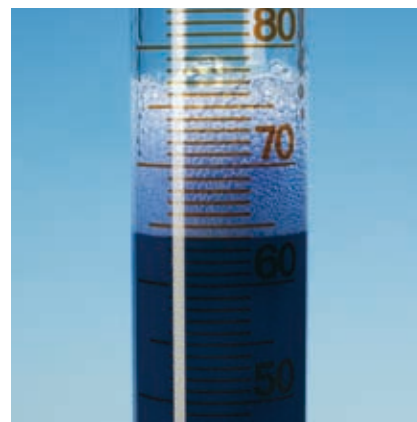


figure 12

### Application with large Pore Roller



figure 13

### Brush Application



figure 14

## Products and Applications

### BYK Additives

Additives are used during the production of coatings, printing inks and plastics to optimize the production process and to improve the quality of the final product.

#### Product Range Additives

- Additives to improve surface slip, leveling and substrate wetting
- Adhesion Promoters
- Defoamers and air release agents
- Foam stabilizers
- Processing additives
- Rheological additives
- UV-absorbers
- Viscosity depressants
- Waxes
- Wetting and dispersing additives for pigments and extenders

#### Application Areas

- Ambient curing resins (FRP)
- Architectural coatings
- Automotive OEM
- Automotive refinishes
- Can coatings
- Coil coatings
- Color masterbatches
- Industrial coatings
- Leather coatings
- Marine paints
- Molding compounds
- Paper coatings
- Pigment concentrates
- Polyurethane foams
- Powder coatings
- Printing inks
- Protective coatings
- PVC plastisols
- Thermoplastics
- Wood and furniture coatings

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