Defoamer and Air Release Agents

Welcome to the interactive world of BYK additives. This multimedia “Defoamers and Air Release Agents” brochure has been designed to support your work, offering interactive graphics, fascinating animations, and videos to show the chemical processes.
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What is foam?

Foam is always unwanted in a coating. Foam can occur during the coating manufacture and results in the production vessels not being filled optimally. It can cause problems when filling containers with the coating or – and this is where the majority of problems occur – it can cause surface defects during coating application. The foam not only affects the visual appearance, it also reduces the protective function of the coating. For these reasons, a defoamer is an integral component in the formulation of a coating system.
Virtually all the components in the coating formulation can influence foaming behavior positively or negatively. The coating substrate and method of application also have an impact on foaming behavior. A coating cannot be "generally" defoamed. For example, the coating surface may be fine for a spray application, but when using the same coating system on a curtain coater there may be issues with foam.

As we are focusing on coatings, we only deal with liquid foams and these are defined as a fine distribution of a gas (generally air) in a liquid. A characteristic feature of this type of foam compared with other physical states is the extremely large interface between the gas and the liquid – a lamella that separates the gas bubbles from each other. For energetic reasons, each liquid endeavors to keep its surface as small as possible, i.e. a foam is always a higher energy state than the liquid phase and is only made possible as a result of foam-stabilizing effects. As soon as they are produced, the gas bubbles in the liquid phase rise to the surface. According to Stokes’ law, the ascent rate \( v \) is dependent upon the radius \( r \) of the bubbles and the viscosity \( \eta \) of the liquid.

Stokes’ Law

\[
V \sim \frac{r^2}{\eta}
\]

Drainage Effect

When the gas bubble has reached the surface, liquid drains out of the foam lamella, i.e. the thin liquid film around the gas bubble (drainage effect). The lamella becomes increasingly thinner and below a thickness of approx. 10 nm the lamella tears and the foam bubble bursts open. If the processes take place as described, there is no problem with foam as no stable foam bubbles are produced; this is the case, for example, in pure liquids: pure liquids therefore do not foam.
For stable foam bubbles to produce, **foam-stabilizing substances** must be present in the liquid phase. In general, these are surface-active substances (surfactants), which are characterized by the fact that they contain hydrophobic and hydrophilic chemical groups in the molecule. This structure makes it possible for them to orientate at the liquid/gaseous interface, **reduce the interfacial tension** and thereby create the requirements for stable foam. Every coating formulation (whether aqueous, solvent-free or using organic solvents) contains a multitude of these types of surface-active substances of the most diverse chemistry and origin. For this reason, foam formation should be expected, in principle, in every coating system.

If you observe the life history of a foam you will establish that it loses liquid over time due to the described drainage effect, thereby changing its structure. Shortly after being produced, foam is characterized by still containing a relatively high level of liquid; this type of foam is therefore referred to as “**wet foam**” or “spherical foam” because the gas bubbles are still spherical and barely deform against each other. The liquid then drains out of the foam lamellae (drainage effect), the lamellae become thinner, the gas bubbles move closer together, deform against each other and become polyhedra. This foam is now called “**dry**” or “**polyhedral foam**”. 

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**Wet and Dry Foam**
As the foam lamellae become increasingly thinner, this drainage effect would cause the foam to collapse if there were no opposing effects. One of these effects comes from the chemical structure of the **foam-stabilizing substances**, the surfactants. In aqueous systems, the hydrophilic groups are ionically constructed. The two interfaces of a foam lamella, which are covered with surfactants, come increasingly closer when the liquid drains away until eventually they interact across the lamella. The like electrical charges repel each other, further drying and therefore collapse of the foam is prevented by the electrostatic repulsion between the surfactant molecules.

**Drainage Effect**

**No Stable Foam in Pure Water**

A member of [ALTANA]
Another stabilizing effect results from the elasticity of the foam lamellae. If the lamellae are stretched slightly, this stretching causes a drop in the surfactant concentration in the interfaces of the stretched region as the same number of surfactant molecules is then distributed over a larger surface. A reduction in surfactant concentration at the surface, however, causes an increase in surface tension, which causes the lamella to return to an energetically favorable state. This difference in surface tension ($\gamma$) is compensated for by the system by a mixture of water and surfactant being discharged from the body and surface of the lamella into the previously stretched region of the lamella. This special foam-stabilizing effect is called the Gibbs-Marangoni effect.
Generally, as potentially foam-stabilizing substances cannot be avoided in coating formulations, defoamers are used to prevent foaming despite the presence of these substances, or to destroy any foam produced as quickly as possible.

Defoamers are liquids with low surface tension that need to essentially fulfill three conditions:

- they need to be insoluble in the medium being defoamed
- they need to have a positive penetration coefficient, and
- a positive spreading coefficient.

If the penetration coefficient is positive, the defoamer can penetrate the foam lamella. If the condition of a positive spreading coefficient is also met, the defoamer is able to spread at the interface after penetrating the lamella. By spreading at the interface of the foam lamella, the foam-stabilizing surfactants are displaced, and the elastic lamella that is stable to interference is replaced by a film with lower cohesive forces.

Penetration coefficient
\[ E = \gamma_F + \gamma_{int} - \gamma_D \]

Wetting of solid particles
\[ S = \gamma_F - \gamma_{int} - \gamma_D \]

Defoamer
\[ E > 0 \text{ and } S > 0 \]

\( \gamma_F \) = surface tension of the liquid
\( \gamma_{int} \) = interfacial tension liquid/defoamer
\( \gamma_D \) = surface tension of the defoamer
Defoamer destabilizes the lamella (dewetting)
Hydrophobic particles destabilize the lamella

Defoamer destabilizes the lamella (spreading)
In addition to particles from hydrophobic silicas, BYK has developed two particle technologies that are based on polyureas and polyamides.

Polyurea particles are characterized by their better defoaming effect and by two further benefits:

1. Polyurea is synthesized from liquid reactants in situ in the carrier oil, which achieves substantially smaller particles and a better resistance to settling. The defoamer itself has better storage stability.

2. The adsorption capacity for surfactants is greater as a result of the larger specific surface, thereby ensuring optimum defoaming, even if the coating is stored for a long period.

Technologies based on polyamide particles are also beneficial as they can be used for applications with food contact. In certain applications they also achieve greater efficiency.

Another key feature of all defoamers is their targeted and controlled incompatibility with the medium that is to be defoamed. A defoamer that is too compatible does not migrate into the foam lamella specifically, it is present in the entire coating film; the defoaming effect is then either low or non-existent. Too much incompatibility causes problematic coating defects such as turbidity or cratering. Choosing the correct defoamer is therefore a kind of “balancing act” between compatibility and incompatibility. This situation is shown graphically in the following figure: too great an incompatibility causes a foam-stabilizing instead of a defoaming effect. The optimum level is found when good defoaming is achieved without defects (turbidity, cratering).

Selecting a defoamer therefore depends on the time of addition, the duration and incorporation method (shear forces), and the dosage in the coating formulation. **All of these parameters have an impact on the distribution** and therefore on the droplet size of the defoamer in the coating formulation. They therefore influence its effectiveness. If the dispersing process is inefficient and causes the formation of droplets that are too large, the coating suffers from surface defects. If dispersion is too great, the defoamer droplets are too small and their behavior in the coating formulation is too “compatible”, decreasing the effectiveness.

For **defoamers with especially high activity**, which are present as concentrate, the defoamer droplets need to be created in situ. This can be caused, for instance, by the defoamer in the coating formulation being finely distributed in the millbase at high shear force. For **defoamer emulsions**, in which the emulsified droplets are already finely distributed in the water, the defoamer can be added to the coating formation at the low shear forces that are usually used during the letdown.
As a result of the multitude of different coating systems, there is no “one” defoamer that is optimally suited to all formulations. To ensure that a suitable product can be provided for any purpose, a range of defoamers is required. The defoaming effect can be finely adjusted by varying the dosage: In general, better defoaming is achieved the more defoamer is used. However, this may also increase the defects or rather these may become more visible. Reducing the dosage prevents film defects, though the defoaming effect may, in some circumstances, not be sufficient.

The term “defoaming” is frequently used to describe the removal of gas bubbles from the coating. However, in certain cases the terms “defoaming” and “air release” should be differentiated. First, the gas bubbles need to reach the surface. Removing the foam bubbles that are at the surface is called defoaming. Defoamers are only effective at the surface where they eliminate the air bubbles located there. In comparison, air release agents take effect throughout the coating film.

Defoaming and Air Release

Foam at the surface. Defoamers destabilize the foam bubbles. Air inclusions in the coating film. Air release agents accelerate the migration of bubbles to the surface.
Small micro bubbles (microfoam) can be entrapped in the coating film. This happens particularly when the film thickness and the viscosity of the formulation is high, hindering the rising of the small bubbles to the surface (see Stokes’s law here above). The internal pressure in small bubbles is higher compared to the external pressure and this phenomenon will cause the air to diffuse out of the bubbles into the coating. During the drying process the small micro bubbles get smaller and literally shrink and disappear. This dissolution process can be followed by a camera linked to a microscope.

This diffusion process of the air ends, however, if the bubble is stabilized as a result of surfactants being adsorbed by the bubble walls. As a result of their surface activity, the mechanism of action of air release agents therefore consists of an orientation at the interface between liquid and air and in the removal of stabilizing surfactants at the interface, enabling dissolution to take place. As it is not always possible to differentiate between these two effects in practice, it can be difficult to establish to what extent an additive is effective as a defoamer or an air release agent.

For this reason, we will use the term “defoamer” in the following even though in specific cases “air release agent” would actually be the correct terminology. In the following, we will primarily illustrate the chemistry of BYK defoamers in aqueous and solvent-borne systems. They can be sub-divided into the following groups:

- mineral oil defoamers
- silicone defoamers
- silicone-free polymer defoamers
Mineral oil defoamers consist of approximately 85–95 % mineral oil and 1–3 % hydrophobic particles. They also contain emulsifiers, biocides and other performance-enhancing ingredients such as modified polysiloxanes. Aliphatic mineral oils are used as the carrier oil.

Emulsifiers are required in defoamers to ensure efficient dispersion of the particles in the mineral oil. They also make it easier to incorporate the defoamer in the coating formulation. As alkylphenol ethoxylates (APEO) are no longer permitted on grounds of health protection, modern mineral oil defoamers contain APEO-free emulsifiers.

In particular, high-quality defoamers for high-gloss emulsions frequently contain small amounts of a modified polysiloxane to improve the spontaneous defoaming effect. Mineral oil defoamers are the most cost-effective products in the defoamer range.

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<th>%</th>
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<tbody>
<tr>
<td>Mineral oil</td>
<td>85-95</td>
</tr>
<tr>
<td>Hydrophobic particles</td>
<td>1-3</td>
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<tr>
<td>Emulsifier</td>
<td>3-6</td>
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<tr>
<td>Modified polysiloxanes</td>
<td>0.5-3</td>
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BYK-030 is the name for the family of BYK mineral oil defoamers. Mineral oil defoamers are primarily intended for matt and semi-gloss emulsion paints and emulsion plasters. They are not suitable for high-quality aqueous industrial coatings as they may cause surface defects (oil separation, gloss reduction). Furthermore, they should not be used in solvent-borne systems as a result of their inadequate leveling properties.
Silicone defoamers are defoamer fluids with a particularly low surface tension, which contain polysiloxanes as the primary active substance. However, when selecting a polysiloxane, its structure is critical. For instance, the relatively short-chained polysiloxanes that are used as silicone surface additives stabilize foam but have no defoaming effect. Whether a polysiloxane has a defoaming or foam-stabilizing effect depends on its compatibility and solubility in the medium: only incompatible and insoluble polysiloxanes have a defoaming effect.

Polydimethylsiloxanes

This figure illustrates this situation for the pure (unmodified) polydimethylsiloxanes. The parameter here is the molecular weight or the chain length of the silicones. Lower molecular weights stabilize foam, higher molecular weights are already so incompatible that they cause cratering, and then there are the entirely incompatible hammerblow silicones. The "specific incompatibility" necessary for the silicone defoamers can be achieved in various ways based on the diverse possibilities that silicone chemistry provides.

Modifying the basic silicone chain with different organic side chains makes it possible to control the compatibility. In this way, polysiloxanes become hydrophilic by introducing polyether chains (R1) based on ethylene oxide, thereby becoming more compatible in polar systems in general. Polymers based on propylene oxide result in more hydrophobic structures. Instead of dimethylpolysiloxanes, it is also possible to use methyl alkyl polysiloxanes. Replacing the second methyl group with a longer alkyl chain (R2) results in higher levels of surface tension for the silicone. In general, this means reducing the foam-stabilizing effect.
Introducing perfluorinated organic modifications resulted in so-called fluorosilicone defoamers. These products are characterized by a very low surface tension and a high defoaming effect.

**Silicone Defoamers for Aqueous Systems**

In terms of silicone defoamers for aqueous systems, these are generally emulsions of highly hydrophobic silicone oils. As a result of the silicone matter they are more expensive than mineral oil defoamers and therefore intended for higher-quality coating formulations. Silicone defoamers can also be combined with hydrophobic solids (polyurea) to improve the dispersion of the silicone oil and to increase the defoaming effect. The primary advantage of silicone defoamers compared with mineral oil defoamers is that they do not affect gloss in high-gloss systems and they have no impact on color paste acceptance when using color pastes.

To obtain crater-free coatings it is important to ensure adequate shear forces when incorporating the defoamer. Very incompatible defoamers need to be added at an early stage to the millbase, for more compatible products such as the standard defoamers BYK-024 and BYK-023, the shear forces during the letdown phase are sufficient. The highly compatible defoamer BYK-025 is characterized by being very easy to incorporate; it can be added easily without curtain tears on the curtain coater. The economical silicone defoamers BYK-1610 and BYK-1615 were developed specifically for emulsion paints in the decorative sector. These two products are suitable for replacing the mineral oil defoamers that are predominantly used in emulsion paints and plasters. BYK-1723, BYK-1724, BYK-1611 and BYK-1617 were specifically developed for applications that need to be labeled with the European ecolabels.

### Silicone Defoamers for Solvent-borne Coating Systems

BYK-065 and BYK-066 N are two fluoro-modified polysiloxanes with a broad spectrum of activity. They offer excellent defoaming with a very low proportion of incompatible substances. BYK-070, BYK-088 and BYK-141 are adjusted to be a little more compatible; the active substance in BYK-088 conforms to FDA §175.300 and is specifically designed for aromatic-free formulations.

In addition to the original silicone defoamers there is also the group of silicones with defoaming properties. This always relates to polymethylalkylsiloxanes. They are used when the foam problem is not too great and when the defoaming effect is an additional requirement for providing typical silicone properties to the coating system such as high surface slip and preventing Bénard cells. If their defoaming effect is inadequate, they are combined with silicone defoamers or silicone-free polymer defoamers.
Polymer Defoamers for Water-based Systems

The polymers need to be insoluble in water. It is important for the polymers to have a low surface tension and spread well over the surface. For polymer defoamers in water-based systems, hydrophobic particles are used to improve the defoaming action. Chemically, the particles are based on hydrophobic silicas, polyurea or polyamide.

BYK-012 is a particularly effective polymer defoamer for high-quality aqueous systems. An equally effective polymer defoamer is BYK-016, which is suitable for various applications with food contact.

BYK-1640 was launched on the market as the first polymer emulsion defoamer. As an emulsion, it is more compatible. In terms of defoaming, BYK-1640 presents an alternative to defoamer concentrates.

Polymer Defoamers for Solvent-borne and Solvent-free Systems

Non-polar and branched polymers are well suited to solvent-borne and solvent-free systems as active defoaming agents. The polymer needs to be active at the surface and interfaces. The compatibility and polarity of the polymers can be adapted accordingly by selecting the molecular weight or monomer.

BYK-052 N is the standard product for polymer defoamers in solvent-borne systems. BYK-1752 is a version of BYK-052 N without aromatic solvents. BYK-354, BYK-355, BYK-361 N and BYK-390 cannot remain unnamed in this discussion. These products, though primarily acrylate-based leveling additives, are also used frequently in numerous systems as defoamers or air release agents. BYK-390 and BYK-392 are recommended for preventing boiling marks in baking coatings.

Silicone-free Polymer Defoamers

It is not only worth considering polysiloxanes as defoamers, there are also other polymer compounds that have a defoaming effect as a result of their incompatibility. Finding the right balance between “incompatible” and “compatible” is achieved by selective changes to the polarity and molecular weight (molecular weight distribution) of the polymer structures.
To establish differences between the control sample and the defoamer samples we recommend incorporating air, i.e. generating foam in the coating system in a reproducible way. As all methods relate to comparative testing and are not absolute methods, it is primarily a matter of producing as much or as little foam as is needed to make a reasonable differentiation.

Foam can be produced, for example, by shaking in a measuring cylinder, up and down motions of a perforated disc or blowing in air via a glass frit; the volume of foam produced can then be used as a measurement parameter.

The defoaming effect is the critical selection criterion for a defoamer and there are a variety of test methods used to test this.
In one of the other standard methods, a dissolver is used to stir in air under defined conditions and then the foamed-up material is poured onto an inclined glass plate. During the run-off, you can observe the foam bubbles bursting and assess upon curing, the tendency of the system to foam via the number of remaining foam bubbles. The light transmitted on a light bank makes it possible to see even the smallest foam bubbles.

The test methods described are entirely irrespective of how much later the coating material is processed. Of course, there are also more practical methods; emulsion paints can be easily tested by rolling with a foam roller, whereby using a very large-pored roller can bring the test conditions closer to real-life conditions.
The foaming behavior of architectural coatings can be tested via brush application, whereby you attempt to include as much air in the coating as possible in the handling of the brush, ("stipple test") to similarly create test conditions that reflect practice.

In highly filled systems (such as plasters) it is most useful to evaluate density: the sample that has been defoamed the most has the highest density. In aqueous dispersions, often only the foam behavior of the (diluted) dispersion binder is examined. Consequently, the test is performed quickly but must be considered to be purely a pretest. The final formulated compound contains numerous components that may also influence the foaming behavior and it is therefore essential to perform foam testing in the finished, formulated coating system. The coating should be tested approx. 24 hours following incorporation of the defoamer but also after storage, as defoamers can lose effectiveness over time.
Frequently, it is beneficial to use defoamers in combination with an (acrylate) leveling additive. Once the foam bubbles have burst, the surface quickly smooths preventing the formation of dents and pinholes. Defoamers are effective if they are insoluble in the medium being defoamed and have a certain level of incompatibility. This results in possible side effects of defoamers:

- gloss reduction
- turbidity (in clear coats)
- cratering

As individual defoamer products behave differently in terms of the possible side effects – also dependent on the coating system – the selection of the correct defoamer must also take this aspect into account. Experiments with various quantities of defoamers should of course be conducted, as only in this way is it possible to adjust the balance between the desired defoaming effect and the unwanted side effects. Whether a coating has foam problems is not just dependent upon the formulation, but also to a large extent dependent upon how it is processed and under which conditions as well as the nature of the substrate. In a specific case, you should strive to include the most important of these application parameters in testing, as only then can you achieve meaningful results that can be used in practice.