Defoamers

TEGO® Foamex

Foam is a phenomenon which frequently occurs during the manufacture and application of coatings and printing inks. The formation of foam interrupts, for example, production processes, reduces the effective volumes in the production plant and leads to unnecessary downtimes. Foam also interferes with the application process. In printing, foam can cause the ink reservoirs to overflow and impairs ink transfer from the printing cylinder to the substrate. Dried foam leaves surface defects in the paint film.

The cause of foam is the introduction of gas into the liquid material.

This can occur by:

- mechanical introduction of air during manufacture by stirring and mixing
- displacement of air during wetting of pigments and fillers
- mechanical introduction of air during applications such as rolling, spraying, printing
- displacement of air when coating porous substrates
- chemical reaction such as the secondary reaction of isocyanates with water

Stabilization of the liberated air to form foam occurs as a result of surface-active substances (surfactants) present in coatings and printing ink formulations where they are essential for stabilizing, dispersing and wetting the formulation.

The occurrence of foam must therefore be considered as an undesirable but unavoidable phenomenon in coatings and printing inks. To prevent foam and destroy any foam present, defoamers have to be added to the formulation.

What is foam?

A stable dispersion of gas in a liquid is called foam. If a stream of air is introduced into a liquid, the bubbles produced assume a spherical shape. Since they are lighter than the liquid, the bubbles rise. A gas bubble, which has penetrated a surfactant-free liquid, has only limited stability and bursts spontaneously. Air from the bubbles escapes and the liquid previously surrounding the air flows back. Therefore, stable foam does not form in pure, surfactant-free liquids (fig. 1).

In liquids such as paints containing surfactants, the gas bubbles are stabilized by the surfactants. A surfactant film forms around the gas bubble. If these bubbles reach the surface, which is also coated with surfactants, a surfactant-stabilized double layer or duplex film is formed (fig. 2).

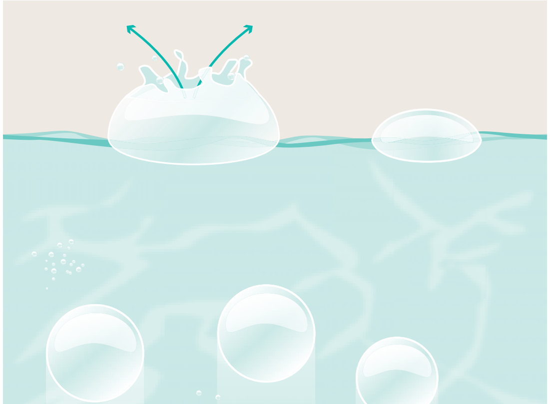


Figure 1: Rise and bursting of air bubbles in surfactant-free liquids

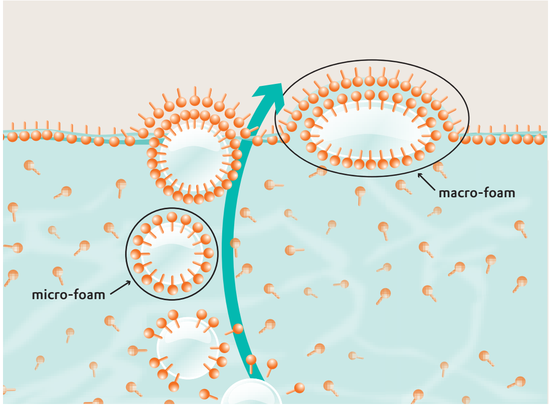


Figure 2: Rise and stabilization of air bubbles in a liquid containing surfactant

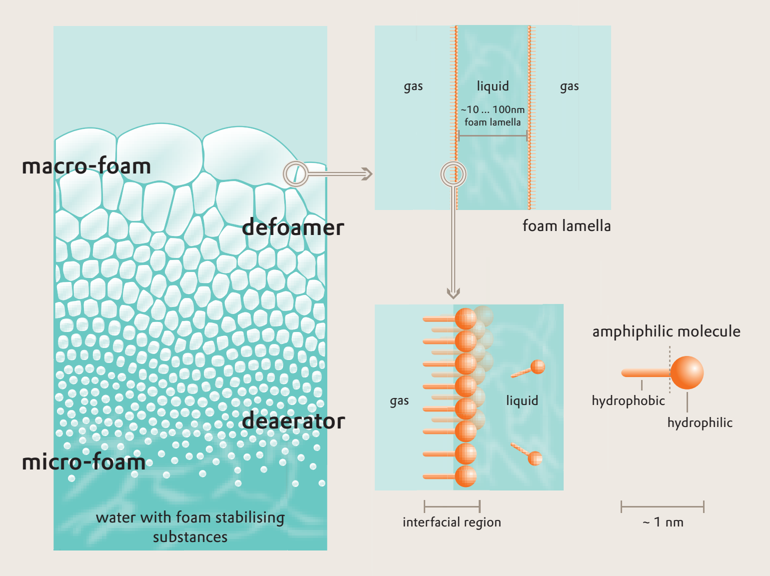


Figure 3: Structure of foam and stabilization of the lamella by surfactants

Duplex films can occasionally be fractions of a millimeter thick. Despite their very small film thickness, they can form very stable foams which are extremely difficult to destroy.

One can distinguish between two types of foam: macro- and micro-foam. Macro-foam is the foam visible on the surface. Foam bubbles generally have a diameter of more than 50 µm and are stabilized by a duplex film. Very fine foam bubbles, which are entrapped in the matrix of the coating film, are called micro-foam. To eliminate macro-foam, defoamers are used; to eliminate micro-foam, deaerators are used. (see "Technical Background Deaerators").

Once the macro-foam bubbles have penetrated the surface, they initially become spherical. In this phase, the volume of the liquid in the foam is greater than the volume of the air in the foam bubbles. Therefore, this foam is termed wet foam. The foam bubbles are still spherical and are stabilized by thick foam lamellas. The bubbles from the liquid cause a continuous rise in the foam head.

The liquid flows out of the foam lamella under gravity. During this so-called drainage process, the proportion of air in the foam increases. The spherical foam is now forced to take on a more stable polyhedral shape. The polyhedral foam is termed dry foam because the volume content of liquid is small. Polyhedral foam consists of very thin (approx. 100 nm) but very elastic foam lamellas, which are stabilized by the surfactant molecules coating the surface. The varying structure of foam is summarized in fig. 3.

Foam stabilization

Drainage would be expected to completely remove the water from foam lamellas which would then collapse on their own accord. In practice, drainage comes to a halt when loss of liquid in the lamellas causes the surfactant concentration to be so high that steric or electrostatic repulsion forces between the surfactant molecules prevent further retraction of the lamella walls. The foam lamella attains a thermodynamically stable state of equilibrium between drainage and surfactant repulsion. Highly thinned foam lamellas are therefore very stable and very elastic. The elasticity of the lamellas can be explained in terms of the Gibbs-Marangoni elasticity. An increase in the lamella surface caused by deformation of the foam lamella leads to a locally reduced concentration of surfactant and, with it, an increase in the surface tension of the lamella. The resultant imbalance results in strong restoring forces towards the energetically more favorable unstretched state of the foam lamella (fig. 4).

How do defoamers work?

Whether defoamers or deaerators are used depends on the type of foam, i.e macro- or micro-foam. To eliminate macro-foam on the surface, prevent large air occlusions and for rapid foam collapse in waterborne formulations, defoamers are preferred. If finely dispersed air needs to be removed from the system, deaerators are preferred. In practice, it is usually not possible to differentiate clearly between defoamers and deaerators. Most defoamers are also effective to some degree as deaerators and the reverse is true. The mechanisms of deaeration are described in the section on deaerators.

Defoamers work by penetrating the foam lamella, destabilizing it and making it burst. Investigations using model systems have resulted in various mechanisms of defoaming being discussed in the literature. From the models, it is possible to deduce the requirements a compound or formulation must meet to be effective as a defoamer.

Requirements for defoamers:

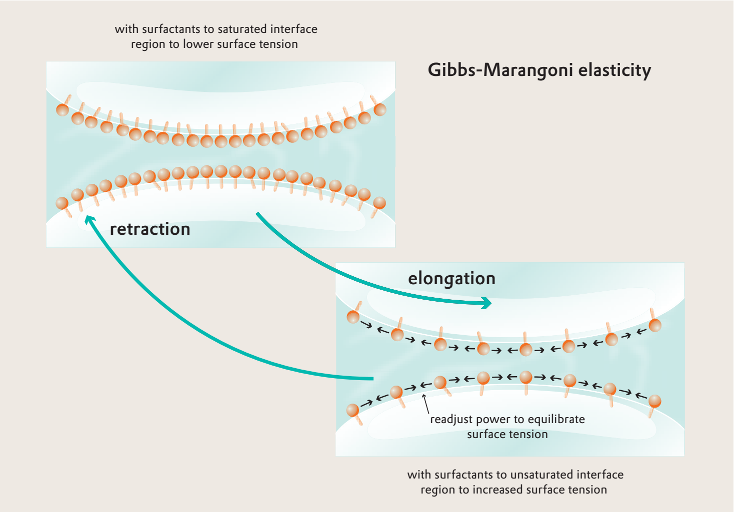
- insoluble in the formulation to be defoamed
- low surface tension
- positive penetration coefficient (E)
- positive spreading coefficient (S) or positive bridging coefficient and dewetting characteristics

Fundamentally, a defoamer must be insoluble in the formulation to be defoamed where it should be present in the form of finely divided droplets. Furthermore, it is necessary for it to be sufficiently compatible with the medium to be defoamed not to cause surface defects such as craters. The choice of defoamer is therefore always a compromise between defoaming performance and compatibility/insolubility.

As already described, defoamers work by penetrating and destroying the foam lamellas. It is a prerequisite that the defoamer is in a position to penetrate the surface of the foam lamella. The first barrier to be overcome when penetrating is the pseudoemulsion film. This is a thin liquid lamella between the rising defoamer droplet and the liquid surface. If the pseudoemulsion film is too stable, a defoamer droplet cannot penetrate the surface and defoaming is not possible.

Once the defoamer droplet has overcome the pseudoemulsion film and penetrated the lamella, its further behavior can be described using the penetration coefficient which can be calculated from the interfacial tensions between the three phases: the liquid to be defoamed, defoamer and air. It describes the force equilibrium between the three phases.

Figure 4: Gibbs-Marangoni elasticity



Only if the penetration coefficient remains positive, does the defoamer remain permanently on the lamella surface. If the penetration coefficient is negative, the defoamer drop can migrate back to the liquid phase.

$$S = \gamma_{w/a} - \gamma_{w/o} - \gamma_{o/a} = \gamma_{w/a} - (\gamma_{w/o} + \gamma_{o/a})$$

spreading coefficients formula

$$E = \gamma_{w/a} + \gamma_{w/o} - \gamma_{o/a}$$

$\gamma_{w/a}$ = surface tension of the foaming liquid

$\gamma_{w/o}$ = interfacial tension between the defoamer and the foaming liquid

$\gamma_{o/a}$ = surface tension of the defoamer

If one assumes the interfacial tension of the foaming medium $\gamma_{w/a}$ is constant, the equation shows that a positive spreading coefficient can only be achieved if the surface tension of the defoamer $\gamma_{o/a}$ is sufficiently small.

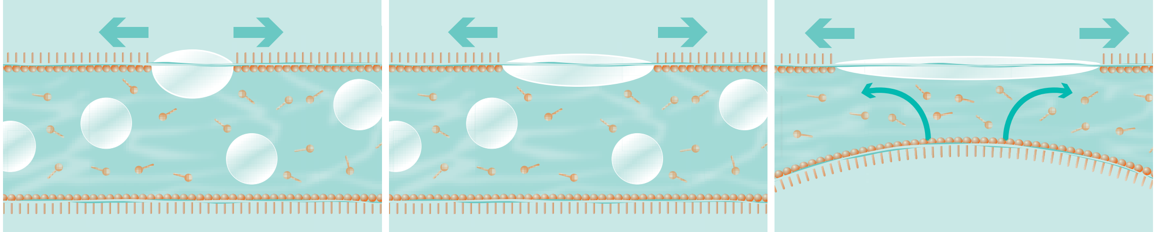
The defoamer droplet may spread after penetrating the lamella. If a defoamer can spread on the surface, it forms a defoamer lens at the lamella surface and displaces the surfactants at this location. As a result, the stability and flexibility of the lamella are impaired and it may collapse. The spreading process leads to flow of the lamella liquid along the direction of spreading. This phenomenon, also known as Marangoni flow, causes a local thinning of the lamella at the location of the spreading defoamer droplet and leads to further destabilization of the lamella. The penetration and spreading of a defoamer droplet is illustrated in fig. 5.

The spreading behavior can be described via the spreading coefficients as the equilibrium of the surface tensions of the three phases with each other. Only defoamer droplets with positive spreading coefficients can spread on the surface of the medium to be defoamed.

The equation for spreading coefficients shows that defoamers can only spread if the sum of their interfacial tensions to air and to the medium to be defoamed is smaller than the surface tension of the foaming liquid.

Defoamers with insufficient spreading power may defoam through another mechanism called bridging. The basic prerequisite is that the defoamer is capable of penetrating the foam lamella and has a positive penetration coefficient. Defoaming by bridging requires that a defoamer droplet which has penetrated the lamella surface must also be capable of penetrating the opposite lamella side. Frequently, this is only possible once the lamella has been sufficiently thinned by continued drainage. In some cases, defoamer droplets become sufficiently large by coalescing with other defoamer droplets for the bridging mechanism to occur. If the defoamer droplet has penetrated both sides of the lamella, a subsequent dewetting or stretching mechanism can lead to rupture of the lamella.

Figure 5: Penetration and spreading of the active ingredient of the defoamer



$$B = (\gamma_{w/a})^2 + (\gamma_{w/o})^2 - (\gamma_{o/a})^2$$

bridging coefficients formula

A basic condition for both mechanisms is for the bridging coefficient of the defoamer to be positive.

Calculation of the bridging coefficients involves the square of the interfacial tensions. The bridging coefficient can only be positive if the interfacial tension between the defoamer and air is sufficiently small.

In the case of the dewetting mechanism, the foaming liquid is not capable of wetting the surface of the defoamer droplet. Consequently, dewetting of the defoamer droplet occurs and the foam bubble collapses. Solid defoaming agents can also act via a dewetting mechanism (fig. 6).

If defoaming takes place via a stretching mechanism, the bridging defoamer droplet marks the weakest point in the lamella. If the lamella stretches, it ruptures at even very low stretching forces on the defoamer droplet (fig. 7).

Figure 6: Film bridging during defoaming

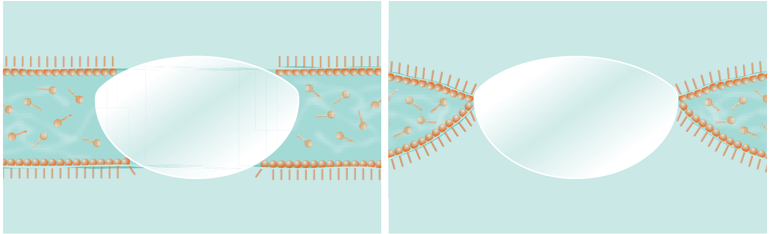
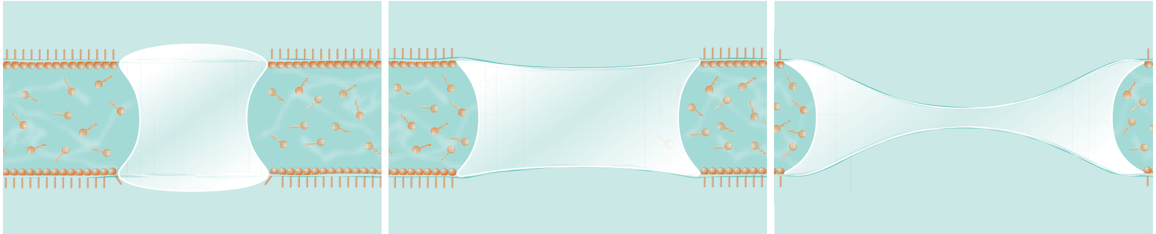


Figure 7: Dewetting during defoaming



Which classes of substance have a defoaming effect in waterborne coatings?

Typical active substances for formulating defoamers for waterborne coatings are: polysiloxanes (silicones), mineral-, vegetable-oils and/or polymers. Particularly effective defoamers tailored to specific applications can be formulated by combining the substances with each other and also by adding fine-particle hydrophobic solids such as silicas.

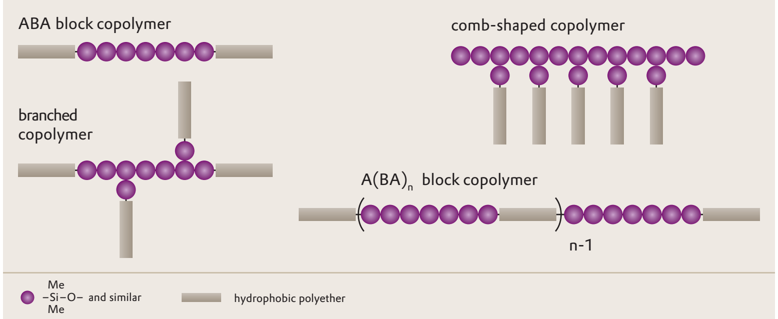
Silicone defoamers (polysiloxanes)

Polysiloxanes and modified polysiloxanes belong to the most widely used group of defoaming substances. An enormous range of defoaming agents is accessible via modification with polyethers or other polymers. The compatibility and effectiveness of these can be adjusted to suit individual coatings formulations. Polysiloxane defoamers have very high spreading characteristics and are highly effective. They are used particularly frequently in modern waterborne coatings and printing inks where high demands are made on defoaming characteristics and surface finish. Applications include pigmented and unpigmented wood, architectural and industrial coatings and printing inks. They do not impair gloss and are distinguished by good compatibility. Modified polysiloxanes are synthesized by forming a Si-O-C or a Si-C link between the siloxane block and the organic modification (fig. 8).

Mineral oil defoamers

Mineral oils, with their high spreading power and high incompatibility, have long been used as defoaming agents. Nowadays, aliphatic mineral oils are used in defoamer formulations. Aromatic oils are increasingly rare because of environmental and physiological considerations. Mineral oils are frequently used in the architectural paints and printing inks sectors. When used in waterborne formulations, where high demands are made on the gloss of the finish, mineral oils frequently reach their limits since they tend to impair gloss or cause other surface defects.

Figure 8: Typical polyether siloxane structures



Vegetable oil-based defoamers

As renewable raw materials, vegetable oils are increasingly important in the formulation of defoamers. They exhibit high incompatibility and have very similar properties to those of mineral oils. They are used mainly in architectural paints but are increasingly important in other sectors.

Polymer-based defoamers

Examples of polymer-based defoamers include modified fatty acids, polyethers or modified amides. The polarity of the defoamers can be adjusted via the composition of the polymers. The effectiveness of polymeric defoamers is frequently inferior to that of other substances. However, the wide choice of polymeric defoamers enables the effectiveness and compatibility of the defoamer to be precisely adjusted for very critical coatings systems. Therefore, polymeric defoamers are frequently used in formulations where other defoamer technologies are too incompatible.

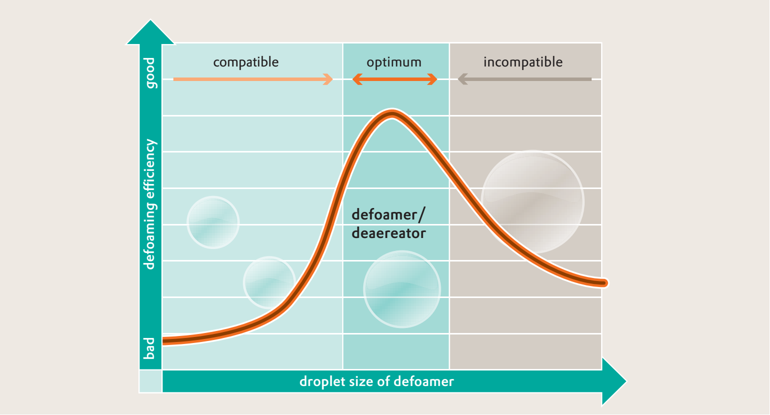
How are defoamers incorporated?

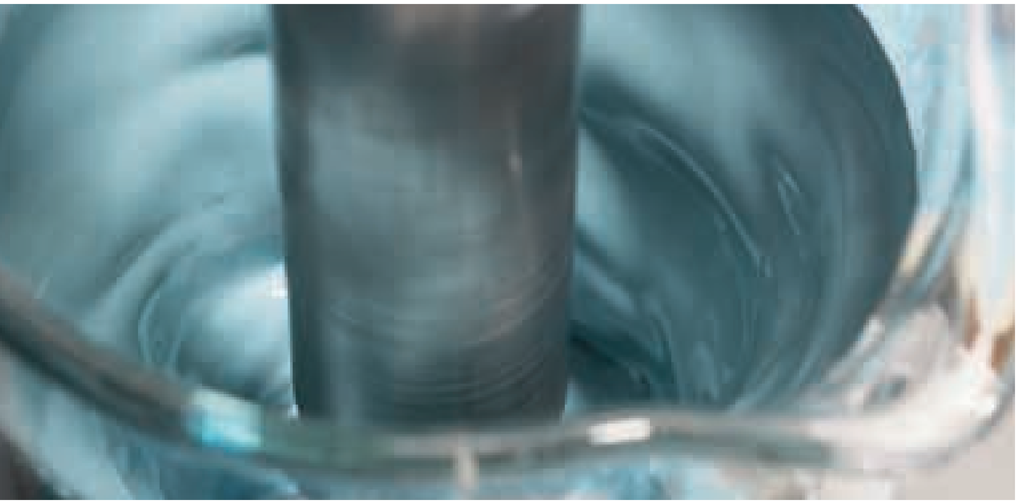
Choosing the method of incorporating a defoamer is largely dependent on the form in which it is supplied. Common forms are defoamer emulsions or concentrates.

In defoamer emulsions, the active substance is already finely distributed in an emulsified form. Defoamer emulsions can therefore be incorporated in the formulation using low stirring intensity. They are also suitable for subsequent addition in the ready-to-use formulation. Typical examples of Evonik’s defoamer emulsions for waterborne coatings and printing inks are TEGO® Foamex 805, 815 N, 822, 825 or 1488.

Defoamer concentrates consist mainly of the active defoamer substance. They are water- and solvent-free. In contrast to defoamer emulsions, the defoamer droplets which provide the defoaming effect in the finished coatings formulation must first be generated. This is typically done during incorporation of the concentrate by finely dispersing the defoamer in the coating using sufficiently high shear forces. It is therefore recommended that the defoamer concentrate be added to the millbase. The incorporation conditions can directly influence the effectiveness of the defoamer. Dispersing which is too weak results in defoamer droplets which are too large and causes surface defects. If the defoamer is too strongly dispersed, the defoamer droplets are too small and cannot develop their full effectiveness (fig. 9). Defoamer concentrates from the TEGO product range are TEGO® Foamex 3062, 810, 883 and 8050.

Figure 9: Effectiveness as a function of droplet size





Which tests are recommended for evaluating defoamers?

Decisive criteria for choosing a defoamer are the formulation and application method. Different formulations require different defoamers. Important parameters affecting the formulation include pigment loading or the chemical nature of the binder. The type of application method also affects the incorporation of foam in the coating material and thus the choice of defoamer. Defoamer recommendations from Evonik take into account suitability for particular formulations and application methods. Nevertheless, it is recommended that defoamers are tested in the laboratory before using them in production.

When choosing a defoamer for a formulation, its effectiveness should first be checked in the laboratory. Since defoaming characteristics are strongly influenced by the conditions during manufacturing and application of the paint, it is recommended that the test method permits evaluation under conditions close to those in practice. The method should also include an assessment of possible surface defects that could be caused by the defoamer.

Stir tests

A frequently used method for low to medium viscosity formulations is the stir test in which air is stirred into the formulation with a fast running stirrer. The effectiveness of different defoamers can be compared via the volume of foamed material. It is recommended that the volume of a control sample without defoamer is checked before and after the stir test.

Flow test

In this test, air is stirred into the formulation with a fast running stirrer. The freshly foamed sample is poured onto a surface. The activity of the defoamer can be assessed from the fresh pour-down. After the pour-down dries, the film can be visually assessed for foam and surface defects. The flow test frequently complements the stir test and is similarly suitable for low to medium viscosity paints.

Roller test

The roller test is used for testing paints which are applied with rollers and simulates real application conditions. The paint is applied with a roller to a substrate and foaming during application is assessed. Surface defects caused by foam, incompatibilities or air occlusions in the coating can be assessed on the dried paint film.

All procedures are shown in videos on our homepage.

FAQs:

We use TEGO® Foamex 810 in a pigmented UV wood finish and sometimes have isolated craters on the application unit. Unfortunately, we cannot reproduce this defect in the laboratory. What can we do?
One way of eliminating craters is by adding a wetting agent such as TEGO® Wet 270 or TEGO® Twin 4100 in amounts of 0.1% to 0.4%.

We manufacture various interior paints. The PVC ranges from 50% to 80%. We also use various binders in these paints. At the moment, we are also using a variety of defoamers. Is there a defoamer which is effective in all paints?
Foam formation and stabilization are usually caused by a mix of emulsifiers and stabilizers from the binder and other surface active substances added directly or indirectly via other raw materials for which the defoamer is suited. Therefore, there cannot be a universal defoamer which always functions in all formulations. However, empirical experience has shown that certain defoamers are well suited for individual areas of application. TEGO® Foamex 1488 or TEGO® Foamex 855 or TEGO® Foamex K 8, for example, perform well over a wide spectrum in the PVC range between 50 to 80% and in typical binders for this range of PVC such as styrene acrylic or vinyl acetate copolymers.

Can defoamer emulsions be diluted with glycols to mix the defoamer into coatings without compatibility problems?
We basically recommend adding defoamer emulsions in the form supplied. Diluting with solvents can destabilize the emulsion and cause it to break.

What types of pumps are suitable for conveying defoamer emulsions?
Defoamer emulsions should, in principle, be conveyed with low-shear pumps. Continuous stirring or pumping should be avoided as this can cause changes in or destabilization of the defoamer emulsion.