

Deaerators

TEGO® Airex



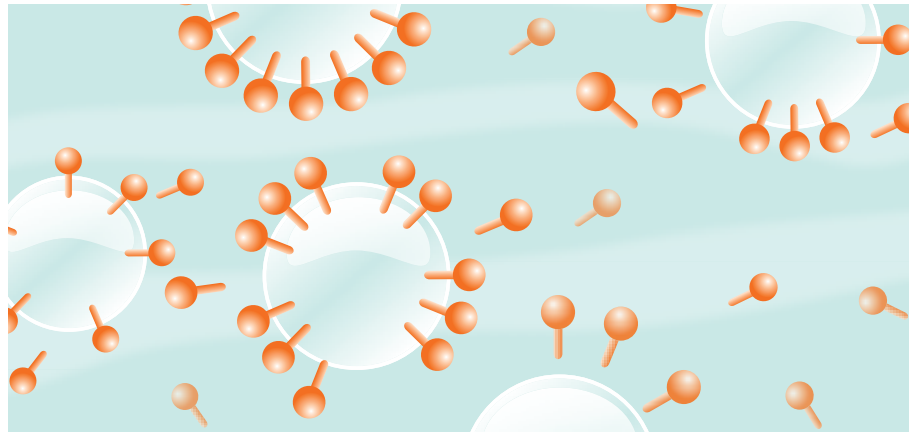


Figure 1: Surfactants orient themselves at the liquid/air interface

Foam – a well-known problem

Foam is one of the most common problems which a formulator must consider when developing coatings and printing inks. It is particularly important in waterborne, radiation-curing, solvent-free and high solids formulations.

Foam is a stable distribution of small gas (usually air) bubbles in a liquid. Pure liquids, however, do not foam. A stable foam can only occur when substances with a surfactant structure are present in the liquid.

Surfactants, with their hydrophilic and hydrophobic regions, orient themselves preferentially at the liquid/air interfaces. A liquid with included or incorporated air has such interfaces. Surfactants orient themselves at this interface and thus stabilize the air bubbles producing stable foam.

Not all foams are the same

There are two types of foam: micro-foam and macro-foam. However, it is frequently difficult to distinguish easily between these foam types as they often occur together as a “foam problem.”

In principle, it is possible to classify macro- and micro-foam. The former is found in, for example, the coating film surface, the latter is found within the coating film. Both types of foam can be distinguished in the liquid coatings material and in the dried/cured coating film.

Macro-foam bubbles in liquid paint are generally air bubbles surrounded by a duplex film of a surfactant double layer. Two liquid/air interfaces exist here. Micro-foam bubbles can be described as air inclusions which only exhibit one liquid/air interface. The surfactants also

orient themselves in this interface and “encapsulate” the micro-foam bubble (fig. 1).

The TEGO® Foamex range of coatings additives from Evonik eliminates primarily macro-foam particularly in waterborne formulations. However, depending on the structure of the additive, they are also effective against micro-foam. These products are fully described in the “Technical Background Defoamers”.

TEGO® Airex additives are predominantly effective against micro-foam although they show positive effects when tackling macro-foam. The mode of operation of the TEGO® Airex family is described below.



Figure 2: Waterborne wood coating, airless application

Micro-foam is usually only recognized at second glance

Many coating problems are not thought of as being associated directly with micro-foam. Furthermore, entrapped air is often only recognized with the help of visual aids such as a magnifying glass or microscope.

Turbidity effects or a reduction in gloss in a coating can be caused by micro-foam bubbles, an undesirable effect in, for example, high gloss finishes (fig. 2).

Premature corrosion can be caused by micro-foam bubbles since they reduce the effective film thickness of the coating. Micro-foam bubbles can also cause small pinholes as the coating dries. These are small channels which can reach right down to the metallic substrate. The protective function of the coating is compromised and corrosion can progress more rapidly.

How is micro-foam formed?

Micro-foam consists of small air or gas bubbles in the coating. When present, surfactants orient themselves at the air/liquid interface, i.e. the air or gas bubble, and stabilize it (fig. 1).

Air or gas can be incorporated in the coating film by:

- stirring/mixing/dispersing during manufacture of the coating
- mixing when adding curing agents in 2-pack systems
- application processes such as rolling, dipping, spraying and, most importantly, airless-/airmix-spraying
- release of gas by chemical processes during curing of the coating (e.g. release of CO₂ through reaction of isocyanate with moisture)
- application on porous substrates such as wood or stone (air entrapped in pores rises in the coating)

Besides the surfactants, two further factors play a key role in the formation of micro-foam:

- the viscosity of the coating
- the size of the air or gas bubbles

Micro-foam – relationship between viscosity of the coating and the bubble size

The factors mentioned are closely related by Stokes’ Law which, in simplified form, is:

$$v \sim r^2 / \eta$$

where

v = velocity of rise of the foam bubble

r = radius of the foam bubble

η = viscosity of the coating

(fig. 3).

This means that if the coating viscosity η is relatively high, the rate of rise of the air/gas bubble is relatively small. Air/gas bubbles, particularly in formulations with a relatively high viscosity (e.g. high solids or UV formulations, floor coatings, high build glazes, anti-corrosion coatings), rise slowly to the coating surface. The viscosity of the coating increases as drying/curing progresses. As a consequence, the bubbles remain in the coating film and result in the well-known problem of micro-foam.

However another important relationship is indicated by Stokes’ Law: the size of the air bubble has a far more marked effect on the rising velocity than the viscosity of the coating because the radius of the bubble appears to the power of 2 in the equation.

Fig. 4 shows the rising velocity of an air/gas bubble at constant velocity as a function of its radius, i.e. its size based on Stokes’ Law.

The rising velocity of very large air/gas bubbles increases exponentially. These reach the surface during curing or drying of the coating where they form macro-foam and can be eliminated with the aid of defoamers (see “Technical Background Defoamers”).

This raises the question: What happens with small air/gas bubbles, known as the micro-foam? An answer is given in the next section.

Figure 3: Rising speed depends on viscosity of the paint and size of the bubble

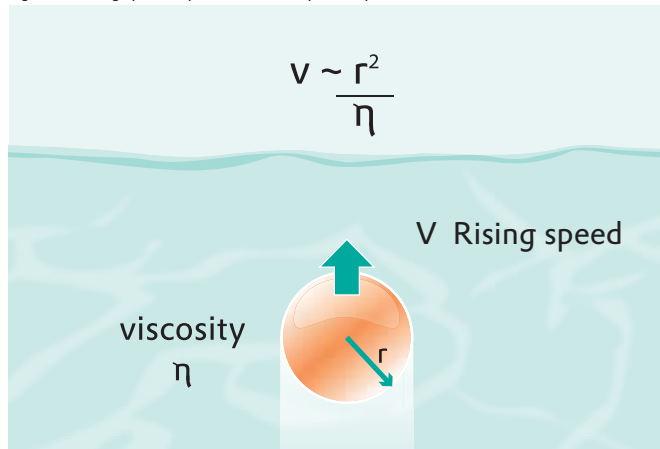
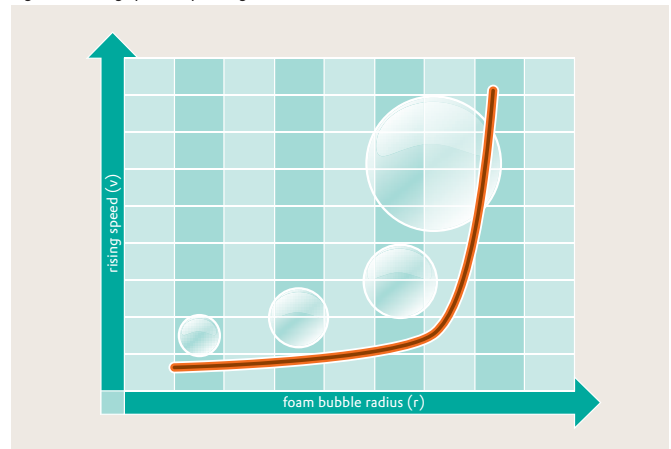
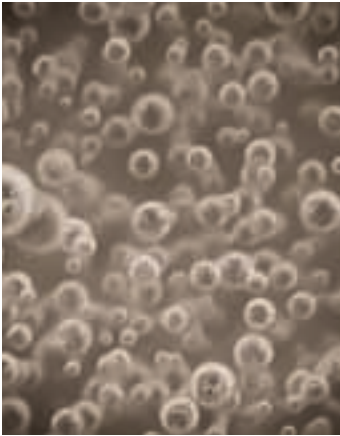
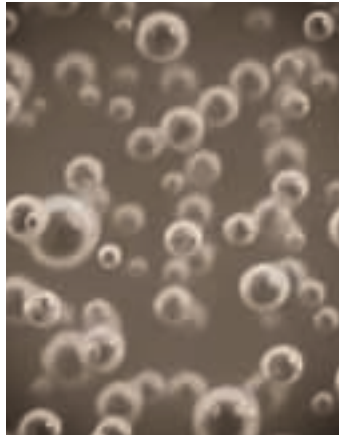


Figure 4: Rising speed depending on the radius of the bubble

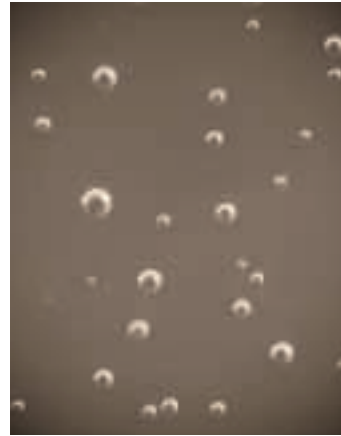




Micro-foam immediately after application



Micro-foam after 10 min



Micro-foam after 20 min

Figure 5: View through a microscope: dissolving of micro-bubbles with time lapse, waterborne on glass, airless application

Can micro-foam bubbles dissolve of their own accord?

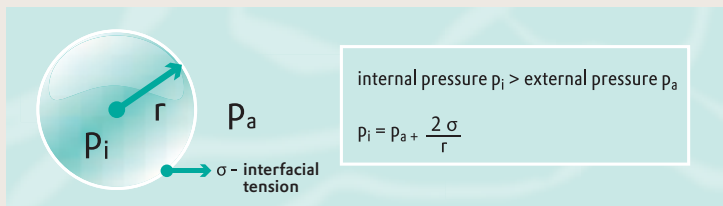
Micro-foam bubbles can disappear of their own accord. They continuously shrink until they disappear. This phenomenon can be easily observed using a microscope during, for example, the drying phase of an airless-applied coating. One can easily track how the micro-foam bubbles change during this time (fig. 5).

At first, there is a mixture of micro-bubbles of different sizes. As drying proceeds, the picture alters. Relatively large micro-bubbles slowly become larger while small micro-bubbles rapidly become even smaller. They literally shrink until they disappear.

The driving force for the shrinkage of the small micro-bubbles is the Laplace pressure of the foam bubble. The Laplace pressure is given by the Young-Laplace

equation, which relates the internal pressure of a micro-foam bubble to the external pressure of the surrounding medium. The smaller the micro-foam bubble, the greater the rise in the internal pressure compared to the external pressure. This pressure difference causes air from the micro-bubble to diffuse into the surrounding medium and dissolve there. Diffusion, and with it, shrinking of the micro-foam bubble continues faster and faster as the bubble becomes smaller.

Young-Laplace equation



The internal pressure of an air bubble is greater than the external pressure as the effect of interfacial tension must be overcome. The ratio of the interfacial tension to the radius of the bubble $2\sigma/r$ is greater the smaller the air bubble. This leads to an increase in the internal pressure P_i . For small air bubbles between 10 and 20 μm diameter, the internal pressure can be 10 to 15% higher than the external pressure.

Laplace Pressure

Derived from the Young-Laplace equation with $P_i = P_a + 2\sigma/r$.

- P_i = internal pressure of air bubble
- P_a = external pressure of air bubble
- σ = interfacial tension
- r = radius of the air bubble

How do deaerators work?

Effective deaerators exhibit a partial or targeted insolubility in the medium to be treated and, ideally, a certain surface activity. The deaerators concentrate preferentially at the liquid/air interface and form, in the ideal case, an additive film around the micro-foam bubble. They thus prevent stabilization of the bubble by surfactants. In addition, the partially insoluble active deaerating substances promote diffusion of air from the micro-foam bubble into the surrounding medium.

Partial or targeted incompatibility of the deaerator means that there is an optimum balance between the effectiveness of the deaerator and the coatings formulation. On the one hand, if the deaerator is too compatible it would not be effective. On the other hand, if it is too incompatible, defects such as craters, fish-eyes or turbidity would occur (fig 6).



Figure 6: Solventborne clearcoat with different deaerators added: from left to right, completely soluble/insoluble/partially or targeted insoluble/incompatible

What substances are effective deaerators?

There is a wide range of chemical compounds which are potentially suitable for use as deaerators in coatings including:

- organic polymers such as polyethers or polyacrylates
- dimethylpolysiloxanes (silicone oils)
- organically modified polysiloxanes, such as aryl-alkyl modified polysiloxanes
- fluorosilicones

These are frequently used for formulating deaerators. Such deaerators are supplied in the following variants:

- as concentrates with 100% active ingredient content
- as solutions in organic solvents
- as aqueous emulsions, specially for use in waterborne formulations

The effect of deaerator formulations is further enhanced by the addition of hydrophobic solids to the above mentioned active substances. Hydrophobic solids used include silicas, ureas or metallic soaps.

Is there a universal deaerator?

A deaerator is effective against micro-foam and, at the same time, sufficiently compatible with the paint, lacquer or printing ink formulation. This means that the deaerator prevents/eliminates micro-foam but does not give rise to, for example, flow problems, fisheyes, craters or turbidity.

This balance is dependent on the coating formulation. Changes, particularly in binder or solvent, strongly influence the effectiveness and compatibility of a deaerator. Therefore, there is no universal deaerator for all coatings systems. Rather, not only the effectiveness but also the compatibility of the deaerator with the coatings system must be checked. The choice and amount of deaerator used in the formulation as well as the method of application play important roles. Preliminary tests are certainly helpful in choosing possible deaerators.

It is essential to confirm the choice of deaerators by evaluation under end-application conditions.

Combinations of additives are helpful

In cases where deaerators are highly effective but cause surface defects such as craters, a combination with substrate wetting agents or surface active additives is recommended (see "Technical Background Slip, Flow and Radiation-curing Additives", and "Substrate Wetting Additives").

Storage stability tests are necessary

High storage stability is expected from many coatings systems. The ideal deaerator should therefore be effective and compatible even after extended storage. Tests under specified conditions are essential (e.g. four weeks at room temperature, 40 °C and 4 °C). In many cases a combination of several deaerators or a deaerator and defoamer is the best choice.

Which test methods for preliminary selection of deaerators have proven themselves?

Test method for low to medium viscosity coatings formulations

50 g of the coating is stirred for 1 minute at a high speed (3,000 rpm) on a dissolver with a disc. This causes air to be incorporated and finely distributed in the coating. Immediately after stirring, the coating is poured down on a transparent polyester film fixed on a glass panel inclined at 25° to the perpendicular. During drying, the coating can deaerate. After drying, the film is assessed visually for bubbles, pinholes (effectiveness) and for possible defects such as craters, fish-eyes, turbidity or flow problems (compatibility) (fig. 7).

Test method for medium to high viscosity coatings formulations

It is difficult to find the ideal deaerator by means of simple preliminary tests, particularly for formulations applied in thick layers by airless/airmix methods. It is more meaningful to carry out a spray

application. After drying/curing, the micro bubble is examined using a magnifying glass or microscope. It can be helpful to document the results using photos.

Evaluation of pigmented coatings can often be difficult because of their poor transparency. In this case, differences in gloss can be used as a criteria: the more micro bubbles, the lower the gloss.

Testing of high viscosity coatings compounds

For coating compounds (e.g. 2-pack floor coatings) the flow test on inclined surfaces is unsuitable. For such formulations, casting of defined film thicknesses (e.g. 3 mm) has proved satisfactory. In this test, the coating material is sheared for 2 minutes at 2,000 rpm to incorporate air.

Directly afterwards, the material is poured onto a PE film. After 10 minutes, one third of the surface is screeded and, after drying/curing, visually assessed for foam bubbles or surface defects. (fig. 8)

In the case of high-build application, the freshly foamed coatings material can simply be filled into a lid (e.g. of a metal paint can or poly beaker) and taken out for assessment after curing (see also video "Deaerating of floor coatings")

Testing of the finest micro-foam

Micro-foam can occur in such a fine form that it is not visible to the unaided eye and examination through a microscope or magnifying glass, etc., is required. However, there are other methods of rendering visible or measuring the very fine pores which can result from micro-foam bubbles in the coating:

Copper sulphate test

The coating is applied in a realistic thickness to a sand-blasted steel panel. After completely drying or curing, about 4 ml of 10% copper sulphate solution is poured into a small watch glass. The panel is placed coated-surface down on the filled watch glass and the apparatus inverted so that the copper sulphate solution can react. After 24 hours, the coating surface is rinsed with water. If there are fine pores in the coating, they show up as red dots. These red marks are elemental copper deposited from the copper sulphate solution while iron has been dissolved from the panel.

Figure 7: Test foil from the flowout test, left with deaerator, right without additives



Pinhole detector

This method is based on the fact that all electrically insulating coatings materials have a higher dielectric strength than air. Pores are detected by arcing between the test electrode and conductive substrate where there is a defect. The presence of pores is shown optically and acoustically. However, the detector can only be used for coatings on conductive substrates.



Figure 8: Specimen of a floor coating

Assessment of entrapped air in coatings for wooden frames or panels

This method is used to assess entrapped air in coating films (after drying/curing) which are applied to wood substrates. Defined cross-sections of the “coating film/wood substrate” are produced and examined microscopically to assess the number and size of micro-foam bubbles. This method is particularly well suited for pigmented formulations.

FAQ:

At what stage in a coatings formulation should the deaerator be added?

Deaerators can be added to the millbase or the let-down. This depends primarily on the incompatibility of the deaerator with the coating system. It is generally true that the greater the incompatibility, the more shear force is required. Some deaerators are excellent as millbase deaerators while others can be used in the let-down or in clear coats. For the ideal point of addition, please see the product data sheets.

How important is the method of application when choosing the deaerator?

The method by which the coating is applied plays a very important role. There are deaerators which, because of their strong incompatibility produce, for example, a break of curtain at the curtain coater machine. In this case, only relatively compatible deaerators should be used.

With airless and airmix application, micro-bubble formation is very strong. This requires especially effective and, therefore, more incompatible deaerators and a good balance between effectiveness and compatibility must be found.

What fundamental ways are there of preventing micro-foam?

There are various possibilities of counteracting micro-foam in coatings and printing inks. The choice of low-foam raw materials or optimally adjusting the coating viscosity can significantly reduce micro-foam problems in a formulation. Production and application of the coating

should be engineered to minimize the entrapment of air in the coatings material. However, parameters such as raw materials, manufacturing regulations and application are usually specified and the room for maneuver is thus significantly restricted. The addition of coatings additives is the simplest way of preventing and eliminating micro-foam.