Deaerators

TEGO® Airex

Foam is a major problem

Foam is one of the most common problems which a formulator must consider when developing coatings, paints and printing inks. Foam is particularly important in waterborne, radiation-curing, solvent-free or high solids formulations. The problem of foam is usually easy to recognize, as when foam bubbles form in a container after filling. Foam is also clearly visible when applying a paint to a substrate by brush or by roller. There are however numerous other problems where the connection with foam is not immediately obvious.

Pinholes encourage corrosion

If the substrate for an industrial coating shows early signs of corrosion the cause may be pinholes in the paint. Pinholes are small channels in the coating which remain when foam bubbles rise too slowly out of the drying paint layer. If these channels reach down to the metallic substrate, moisture and salts can penetrate unhindered resulting in progressive corrosion.

Clouding and loss of gloss caused by small foam bubbles

If a coating does not develop gloss or becomes cloudy immediately after application, the initial response is to suspect incompatibility of the components of the paint. However inspection using a microscope or even a simple magnifying glass reveals that cloudiness or low gloss is sometimes caused by extremely fine air bubbles trapped in the dry paint film.

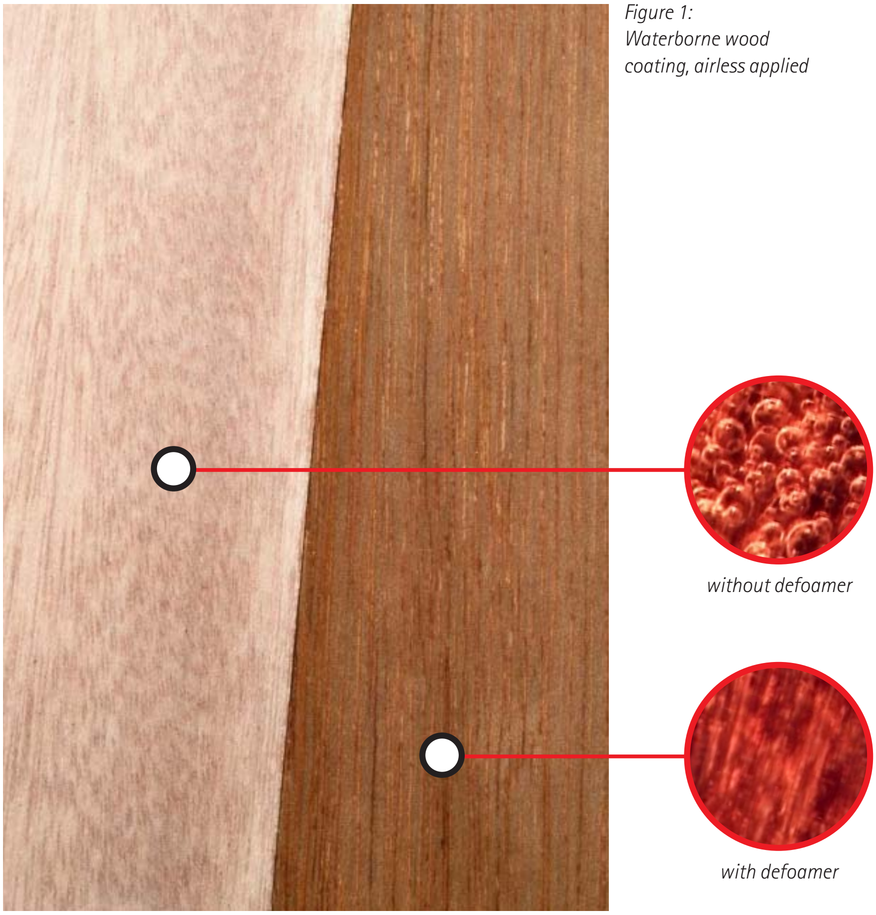


Figure 1: Waterborne wood coating, airless applied

Air inclusions inhibit optimal curing of UV coatings

A great advantage of radiation-curing coatings is that they cure within a few seconds. Oxygen from the air can slow down curing. Inert gas can be used to avoid contact of the coating with air. In spite of this, curing can be affected if foam bubbles containing air are present in the coating. This can be prevented by adequate deaeration of the coating using additives from the TEGO® Airex family.

Two different types of product – TEGO® Foamex and TEGO® Airex

There are two types of foam: micro-foam and macro-foam. However it is often difficult to differentiate these foam types clearly as they often occur together as a "foam problem" in coatings, paints and printing inks. Degussa supplies TEGO® Foamex additives, which primarily remove macro-foam, particularly in waterborne formulations. However, depending on the structure of the additive, they are also effective against micro-foams. These products are fully described in the "Technical Background Defoamers" (p. 44).

TEGO® Airex additives are predominantly effective against micro-foam although they also show positive effects when tackling macro-foams. The mode of operation of the TEGO® Airex family of products and their applications will be described below.

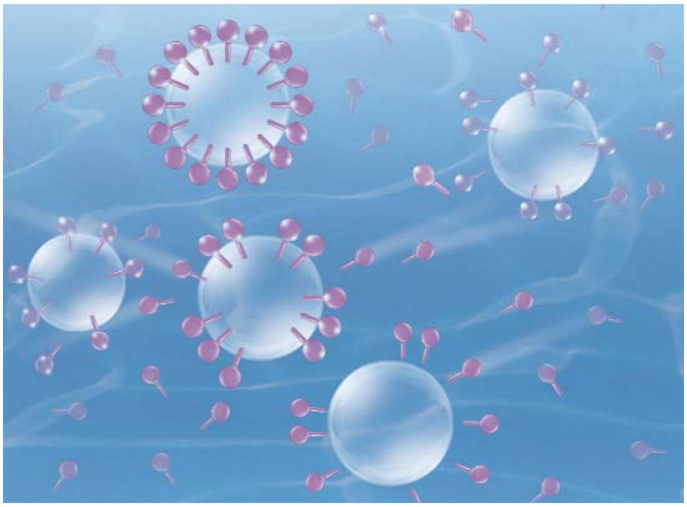


Figure 2: Surfactants orient themselves at the interface liquid/air

What is foam?

Surfactants cause foam

Foam is a stable distribution of small gas bubbles (usually air bubbles) in a liquid system. Pure liquids do not foam. Only if surfactants are present in the liquid can a stable foam occur.

Surfactants with their hydrophilic and hydrophobic regions orient themselves preferentially at the liquid/air interface. Included or incorporated air in a liquid has such interfaces. Surfactants orient themselves at this interface and thus stabilize the air bubbles producing stable foam (fig. 2).

Many raw materials used in formulating paints and coatings contain surfactants which result in foam formation:

- the binder itself (particularly in dispersions and emulsions for waterborne formulations)
- wetting and dispersing additives
- surface or substrate wetting additives
- waxes and wax dispersions or grinding additives such as stearates

Paint viscosity is responsible for foam problems

Viscosity also has a decisive effect on foam formation in paints, coatings and printing inks.

For example, the speed at which foam bubbles rise depends on the viscosity of the paint formulation. According to the simplified form of Stoke's Law the relationship is (fig. 3):

$$\boxed{v \sim r^2/\eta}$$

v = rising speed of the foam bubble
r = radius of the foam bubble
η = viscosity of the paint

This means that air bubbles in paint formulations with a relatively high viscosity η only rise very slowly (small rising speed v). As a consequence air bubbles do not reach the paint surface but remain in the paint layer while the paint cures further or dries physically – a great problem particularly in highly viscous floor coatings or high-build wood varnishes.

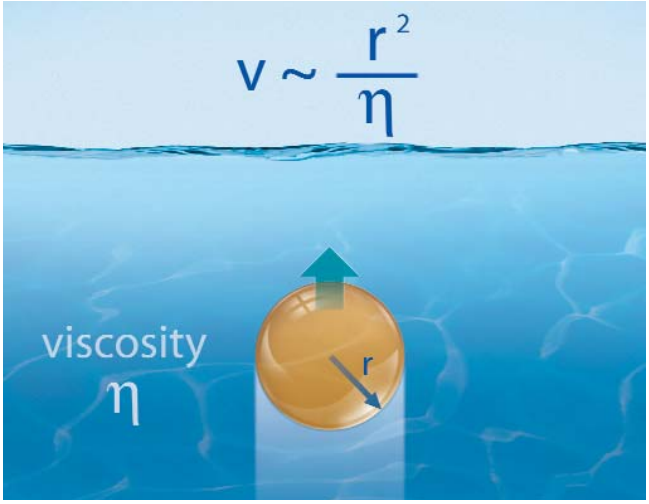


Figure 3: Rising speed depends on viscosity of the paint and size of the bubble

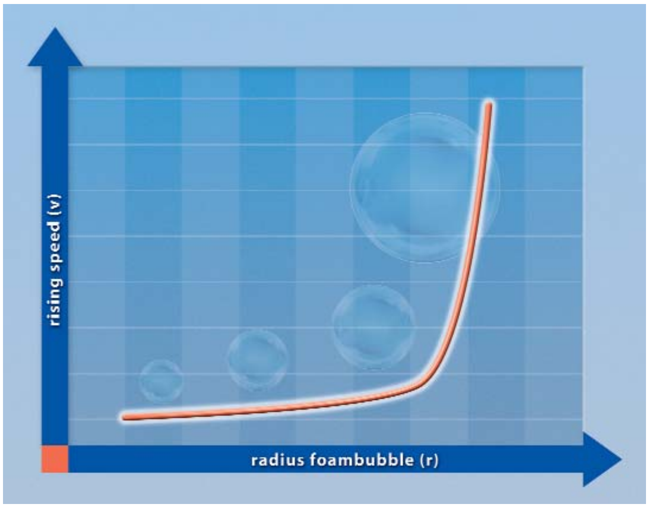


Figure 4: Rising speed depending on the radius of the bubble

Micro-foam and macro-foam – size is the distinguishing feature

However another important relationship is indicated by Stoke's Law: the size of the air bubble has a very marked effect on the rising velocity as the radius of the bubble appears to the square in the equation.

Large air bubbles (>100 µm diameter, but depending on the viscosity) rise very quickly – sufficiently quickly that, during curing or drying, they reach the surface where they form macro-foam (see "Technical Background Defoamers", p. 44).

In contrast, the rising velocity of air bubbles between about 10 and 100 µm diameter is so small that, same viscosity provided, they rise extremely slowly and finally remain in the coating. These small bubbles are called micro-foam (fig. 4).

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 and surround the micro-bubbles.

Micro-bubbles can often only be recognized with visual aids such as a magnifying glass or a microscope. However, for micro-bubbles to occur, air or gas must first have been incorporated into the paint formulation.

Air incorporation can occur by:
- stirring during paint manufacture
- stirring when adding curing agent 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 paint (e.g. reactions of isocyanate with moisture)
- application on porous substrates such as wood, stone or cement floors

How can micro-foam be prevented in paint films?

There are different ways of combating micro-foam in paints, coatings or printing inks. Choice of low-foaming raw materials or adjustment of viscosity to an optimum value can markedly reduce micro-foam problems. The manufacturing and application processes should also be organized so that only a minimum of air is incorporated into the coating material. Nevertheless items such as raw materials and methods of manufacturing and application are usually specified and the room to maneuver is very limited. Addition of additives such as deaerators is the simplest way to inhibit and remove micro-foam.

Can micro-bubbles dissolve of their own accord?

Changes in micro-bubbles in a coating which has been applied by airless techniques can be observed under a microscope during the drying phase (fig. 5).

At first there is a mixture of micro-bubbles of different sizes. As drying occurs the picture alters. Large micro-bubbles become larger while small micro-bubbles become even smaller. They literally shrink until they are no longer recognizable.

The driving force for the shrinkage of the small micro-bubbles is the Laplace pressure of the micro-bubble. The Laplace pressure is given by the Young-Laplace equation. It relates the internal pressure of a micro-bubble to the external pressure of the surrounding medium.

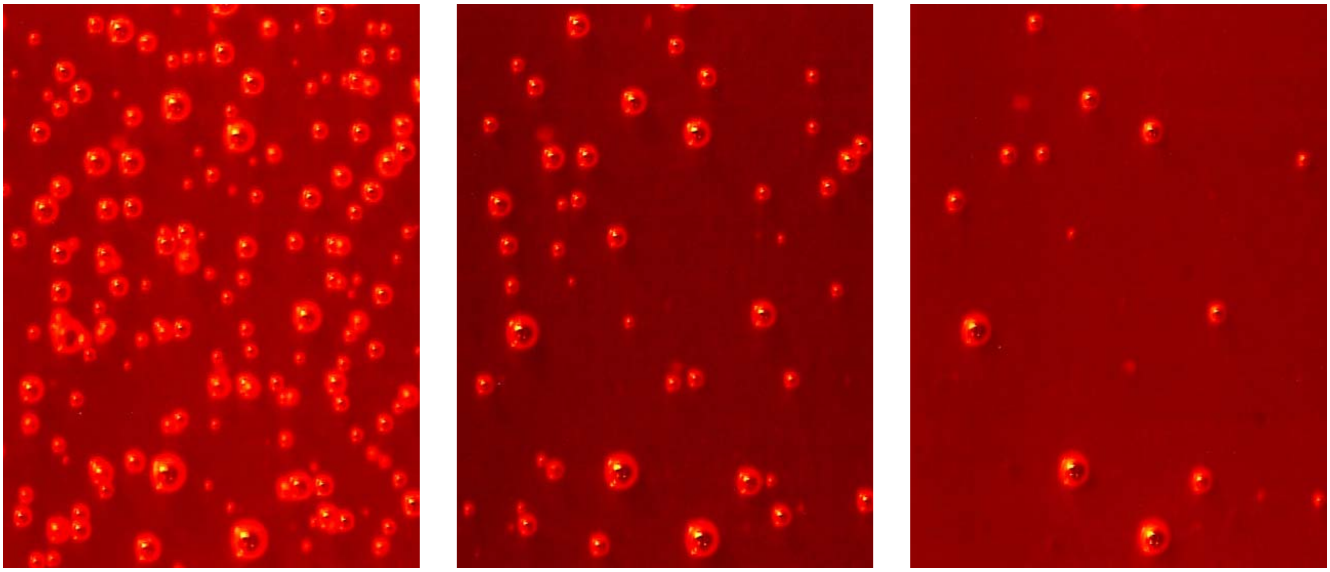
With small micro-bubbles the internal pressure is higher than the external pressure and this pressure difference causes air from the micro-bubble to diffuse into the surrounding medium and dissolve there. Diffusion, and with it, shrinking of the micro-bubble occurs. This becomes faster the smaller the micro-bubble so that small micro-bubbles dissolve.

The air from the small micro-bubbles either remains dissolved or diffuses into larger micro-bubbles whose internal pressure is markedly lower. Larger micro-bubbles can thus grow further.

Laplace Presure:
Derived from the Young-Laplace equation with $P_{in} = P_{ex} + 2\sigma/r$.
P_{in} = internal pressure of air-bubble
P_{ex} = external pressure of liquid surrounding the bubble
σ = interfacial tension
r = radius of the air-bubble

The internal pressure of an air bubble is greater than the external pressure as the effect of interfacial tension σ must be overcome. The ratio of interfacial tension to radius of the bubble is greater the smaller the air bubble. This leads to an increase in the internal pressure P_{in}. For small air bubbles between 10 and 20 µm diameter the internal pressure can be 10 to 15 % higher than the external pressure (fig. 6).

Figure 5: View through a microscope: dissolving of micro-bubbles with time proceeding, waterborne formulation on glass, airless applied



Micro-foam immediately, formulation without deaerator

Micro-foam after 10 min, formulation without deaerator

Micro-foam after 20 min, formulation without deaerator

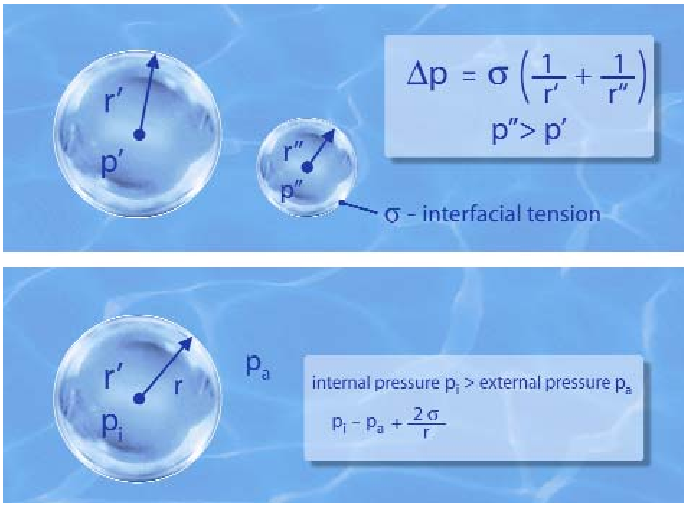


Figure 6: Young-Laplace equation

How do deaerators work?

Effective deaerators must have a targeted incompatibility with the paint formulation so that the deaerator immediately orients itself at the air/liquid interface, i.e. at the micro-bubbles. It is assumed that the deaerator displaces foam stabilizing surfactants there and so promotes diffusion of the air into the surrounding medium. The micro-bubbles become ever smaller until they completely dissolve.

Larger micro-bubbles grow further as air diffuses into them and can rise more quickly to the surface (Stoke's Law). There they break or form surfactant-stabilized foam bubbles (see "Technical Background Defoamers", p. 44).

The additional defoaming effect of a deaerator (destruction of macro-foam) is also intensified if the deaerator contains hydrophobic solids such as silica, urea or metal soaps.

What substances are effective deaerators?

Effective deaerators have targeted incompatibility with the coating system. However it is necessary to find a good balance between effectiveness and compatibility: If the compound is too compatible, it will not exhibit deaerating activity, but if it is too incompatible, there will be defects such as craters, fish-eyes or turbidity (fig. 7).

There is a wide range of chemical compounds which can show targeted incompatibility in coatings systems, e.g.:

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

These are frequently used as deaerators or for the formulation of deaerators. These basic substances are supplied in the following variants:

- as products containing 100 % effective agent
- as solutions in organic solvents
- as waterborne emulsions, specially for use in waterborne formulations

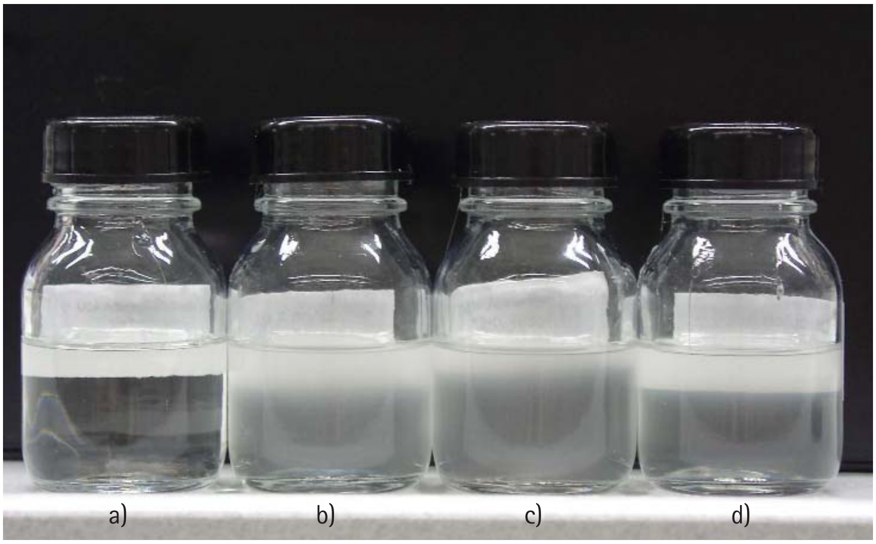


Figure 7: Solventborne clear coat, with different additions of deaerator: a) compatible; b) + c) incompatible; d) targeted incompatible

Is there an ideal deaerator?

The ideal deaerator is both effective and sufficiently compatible with the paint, coating or printing ink formulation. Both effectiveness and compatibility must be tested for each particular coating system. Effectiveness and compatibility are not only dependent on the deaerator itself but also on the quantity used in the formulation. The deaerator most suitable and its optimal concentration should be determined in preliminary investigations as well as in tests made under practical conditions.

Combinations of additives are helpful

Highly efficient deaerators may unfortunately produce surface defects such as craters. This can be avoided by combining them with substrate wetting or surface active additives (see "Technical Background Slip, Flow and Radiation-curing Additives", p. 60, and "Substrate Wetting Additives", p. 68).

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 demanded 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.

Degussa supplies deaerators from the Tego product range for numerous applications thus enabling micro-foam and general foam problems to be effectively combated in waterborne, solventborne, solvent-free, radiation-curing and high solids formulations.

Meaningful test methods for deaerators

Experience shows that simple preliminary tests are helpful in evaluating and choosing deaerators. However these tests do not replace evaluation under end-application conditions.

Test methods for low to average viscosity paint formulations

50 g of the paint is stirred for 1 minute at a high speed (3,000 rpm) on a dissolver with a disc. This causes much air to be incorporated and finely distributed in the paint. Immediately after stirring, the paint is poured down on a transparent polyester film fixed on a glass panel inclined at 25° to the perpendicular. After drying, the film is assessed visually by transparent light for bubbles, pinholes and (if deaerator has been added) by reflected light for possible defects such as craters, fish-eyes or orange peel (fig. 8).

Test methods for medium to high viscosity paint formulations

The following method has proved particularly useful as a preliminary test for formulations which will be applied airless in thick layers: The coating material (50 g) is stirred at a high rotation speed (3,000 rpm) with a dissolver for 3 minutes in order to incorporate air. A coating is immediately applied by doctor blade on glass (300 µm). After drying, the micro-bubbles are examined with a magnifying glass or microscope.

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

Testing high-build coatings

For high-build coatings, e.g. 2-pack floor coatings, the flow test is not suitable. For such formulations it is better to use grid molds with which a defined layer thickness (e.g. 3 mm) can be obtained. Freshly stirred coating compound is added to a mold which has been treated with release agent. After curing, the specimen is removed from the mold and evaluated visually (fig. 9).

However, in many cases the freshly foamed coating material can simply be filled into a lid from a metallic coating container or a plastic beaker and, after curing, evaluated (please see the video "Deaeration of floor coatings").

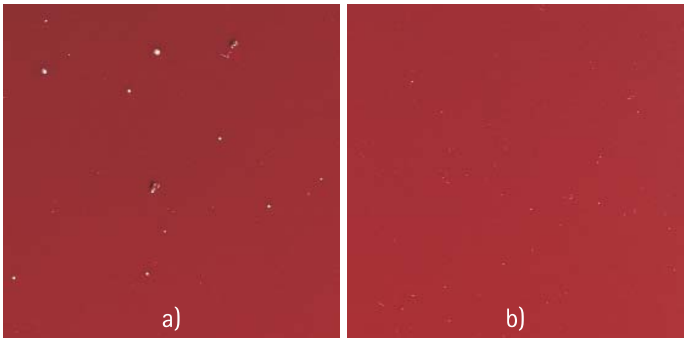


Figure 8:
Test foils from the flowout test
a) without additves,
b) with deaerator

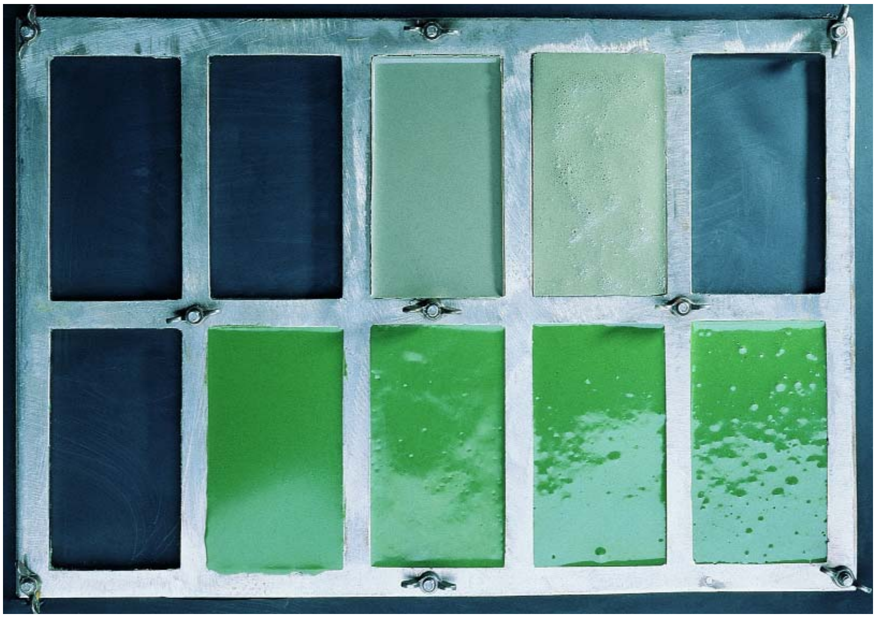


Figure 9: Specimen of a floor coating

Test on the finest micro-foam

Micro-foam can occur in so a fine form that it is no longer visible to the unaided eye. Optical equipment such as a microscope or magnifying glass can be of help. However the following method can render visible the finest pores which occur from micro-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 filled into a small watch glass. The sheet 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 paint 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.

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 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 technical data sheets of the products.

Can deaerators also act as defoamers?

Basically yes. Both deaerators and defoamers work on the principle of targeted incompatibility. If macro-bubbles form, e.g. in low viscosity formulations, deaerators will also orient themselves at this liquid/air boundary. The targeted incompatibility of the deaerator leads to dewetting and the foam bubble can rupture (see also "Technical Background Defoamers", p. 44)

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-applications micro-bubble formation is very strong. This requires especially effective and therefore more incompatible deaerators and a good balance between effectiveness and sufficient incompatibility must be found.