

Surface Additives

Welcome to the interactive world of BYK additives. This multimedia brochure on "Surface Additives" brochure has been designed to support you in your work with interactive graphics, fascinating animations and videos depicting chemical and physical processes.

01

Surface defects

During and after the application of a coating system, surface defects can often occur that affect the optical properties of the coating and its protective function.

Typical **surface defects** are:

- Poor substrate wetting**
- Cratering**
- Formation of Bénard cells, floating**
- Poor leveling, orange peel**
- Air-draft sensitivity**

A key parameter for all these sorts of defects is the surface tension of the materials involved; in particular, differences in **surface tension** lead to the formation of surface defects. Surface tension differences can originate from the system itself (evaporation of the solvent, cross-linking reaction of the binder) or can be caused by external sources overspray or dust particles (contamination of the substrate).

To avoid these surface defects, additives are used to influence the surface tension of the coating and/or minimize surface tension differences. Such products are primarily **polysiloxanes** (silicones) and **polyacrylates** (acrylate additives).

02

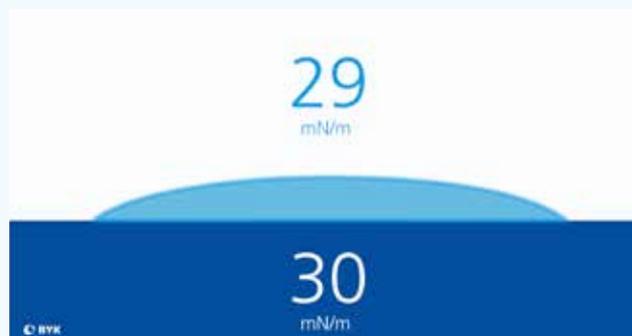
Causes and prevention options

If considerable surface tension differences must be equalized, **polysiloxanes** can be used. Depending on their chemical structure, they can considerably reduce the surface tension of the liquid coating. They can therefore preferentially be used to improve the substrate wetting and as anti-cratering additives. Given sufficient incompatibility with the coating system, polysiloxanes can also have a defoaming effect. Moreover, silicone additives also improve the surface slip of the cured coating film, and can therefore help improve scratch and block resistance.

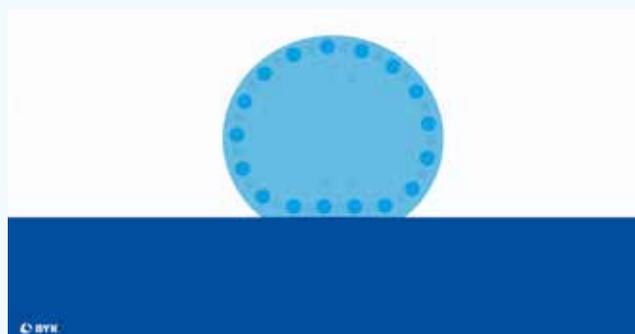
Polyacrylates can only equalize small surface tension differences and either do not reduce or only slightly reduce the surface tension of the liquid coating.

They are predominantly used to improve leveling. However, with sufficient incompatibility, these products can also exhibit defoaming properties. In addition, there is the group of low-molecular weight **surfactants** that are likewise surface active, due to their typical amphiphilic structure (polar/non-polar), and can be used to reduce surface tension.

Surface tension vs. surface energy



Improvement of leveling with additives

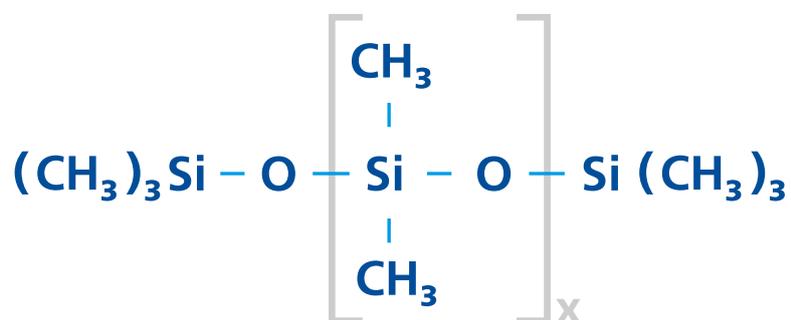


03

Chemical structure of polysiloxanes

Silicone additives, often also referred to as “silicones,” can be used without understanding their basic underlying chemistry. However, it is helpful to outline and understand several of the underlying principles of silicone chemistry. In this way, one can readily learn how to understand and characterize silicone additives. Additionally, the relationship between structural features and resultant properties will become more understandable.

Polydimethylsiloxane

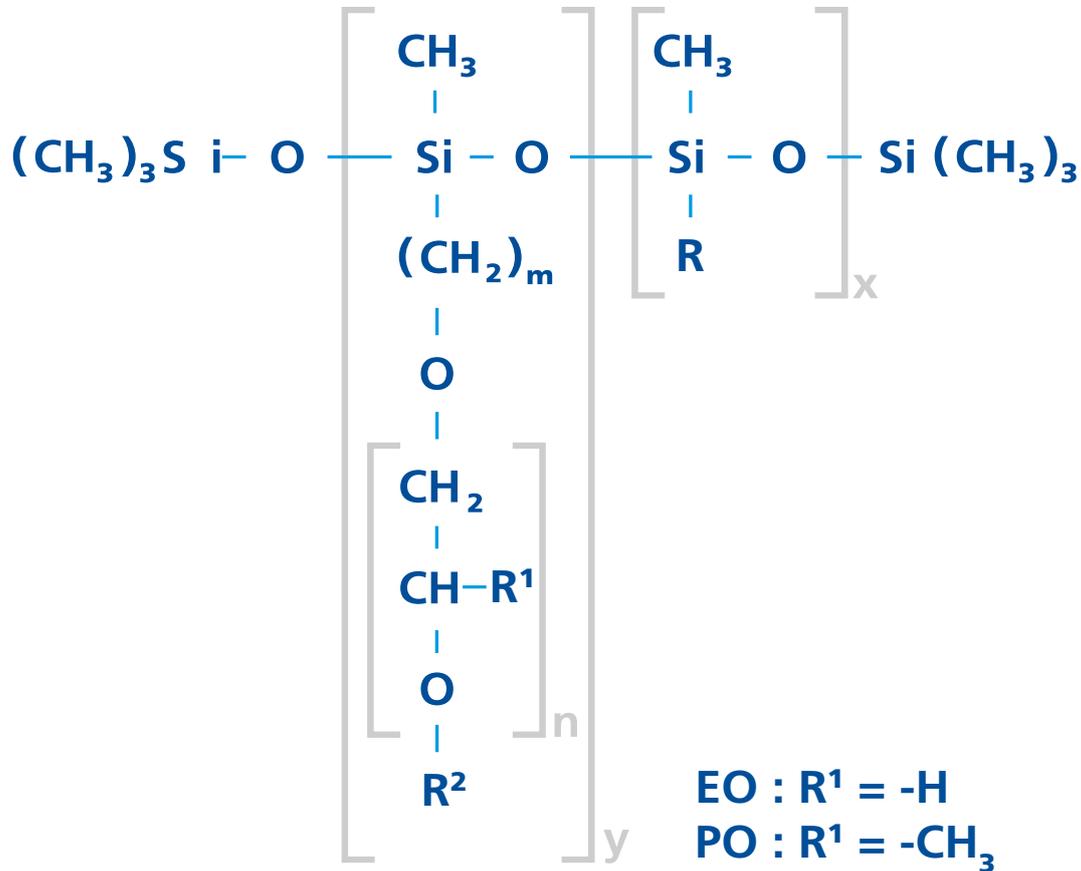


All silicone additives are derived from the basic structure of polydimethylsiloxanes (see figure).

Varying the chain length creates products with very different properties. While short-chained silicones are relatively **compatible** in coating systems and have the typical

silicone properties, such as low surface tension, the long-chained molecules are very **incompatible**, and cause a very definite cratering (hammertone effect). Accordingly, pure polydimethylsiloxanes (silicone oils) are rarely ever used in modern paints.

Polyether modification



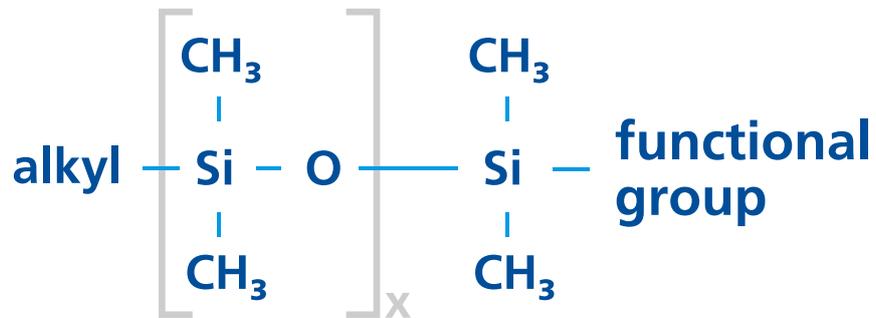
A more elegant method than controlling compatibility by means of chain length is to modify the silicone basic structure by adding side chains.

The majority of silicone additives used in coatings today are such “**organically modified** polysiloxanes.” In the majority of cases, the modification involves **polyether** chains (see figure) which lead to an improvement of compatibility. The degree of compatibility can be controlled by the number of these side chains (i.e. ratio of dimethylsiloxane units to polyether modifications (x;y). At the same time, this also influences the **surface tension**: Generally speaking, the more dimethylsiloxane units, the lower the surface tension. Furthermore, the structure of the polyether chains themselves can also be varied; the key factor here is the **polarity**.

Polyethers consist of ethylene oxide units (EO) and/or propylene oxide units (PO). Polyethylene oxide is very hydrophilic (polar), whereas polypropylene oxide by comparison, is rather hydrophobic (non-polar).

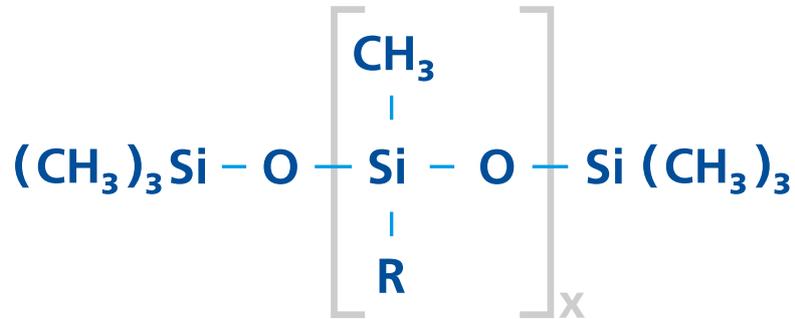
Therefore, the polarity of the entire silicone additive can be controlled via the ratio EO/PO: A greater proportion of EO increases the polarity and the additive is water-soluble and more compatible in polar coating systems. At the same time, however, the tendency toward foam stabilization increases. On the other hand, a greater proportion of PO reduces both the water solubility and foaming tendency.

Silicone macromers



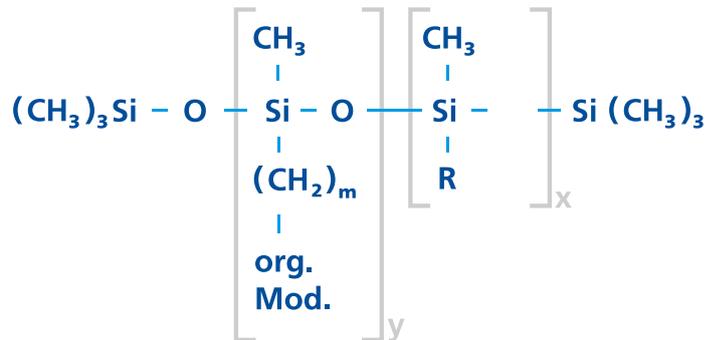
In the synthesis of “silicone macromers” (see figure), the chain length of the silicone block can be very precisely adjusted as compared to **“organically modified polysiloxanes”**. Using the functional group, which might be, for example, an amino, methacryl, vinyl or hydroxyl group, these special components can be further transformed to become active substances with a defined structure. The additives created in this manner have tailor-made properties.

Polymethylalkylsiloxanes



Another method of changing the silicone structure is to replace one of the two methyl groups of the dimethyl structures with **longer alkyl chains**, resulting in polymethylalkylsiloxanes (see figure). Compared with polydimethylsiloxanes, such products clearly demonstrate higher surface tensions, and exhibit less influence on the surface slip. Such silicones are often used as the active substance in defoamers. Just like polydimethylsiloxanes, the polymethylalkylsiloxanes can also be organically modified with polyether chains. In addition to typical silicone characteristics, such silicone additives also exhibit slight defoaming properties.

Other types of modification (e.g. thermostable modified polysiloxane)



org. mod. = aralkyl group



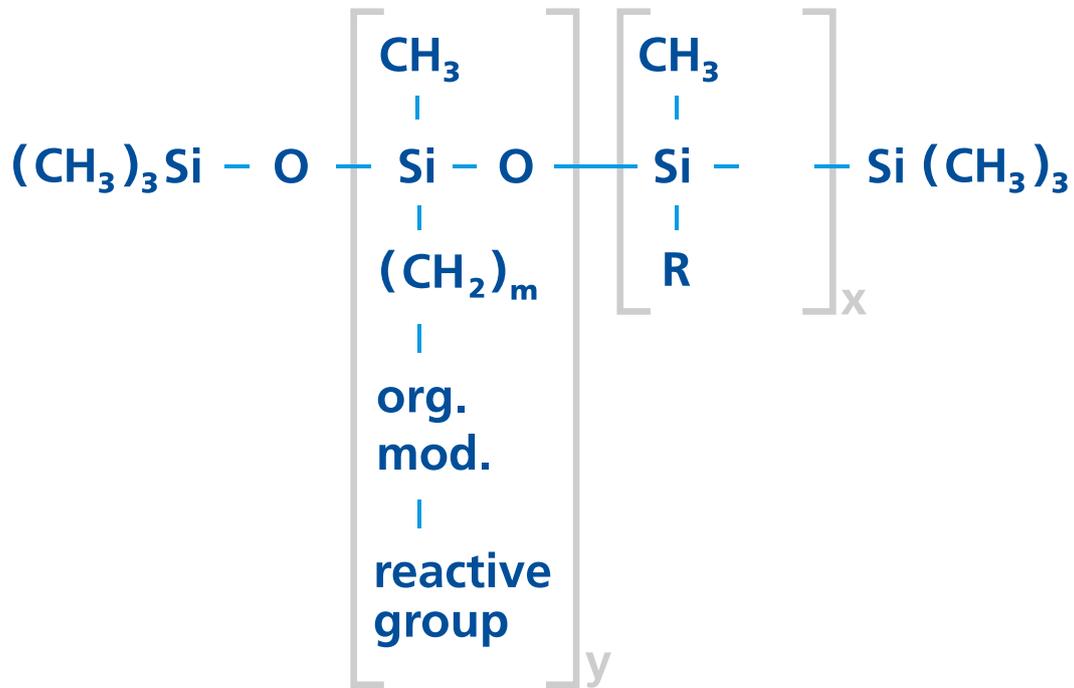
org. mod. = polyester



BYK

Polyether-modified polysiloxanes are thermally stable up to about 150 °C; the polyether chains will decompose at higher temperatures. Through the use of non-polyether structural elements such as polyester and aralkyl groups (see figure), various thermally stable products can be produced. These modified polysiloxanes are thermally stable up to 220 °C and can be used at much higher baking temperatures.

Reactive silicones



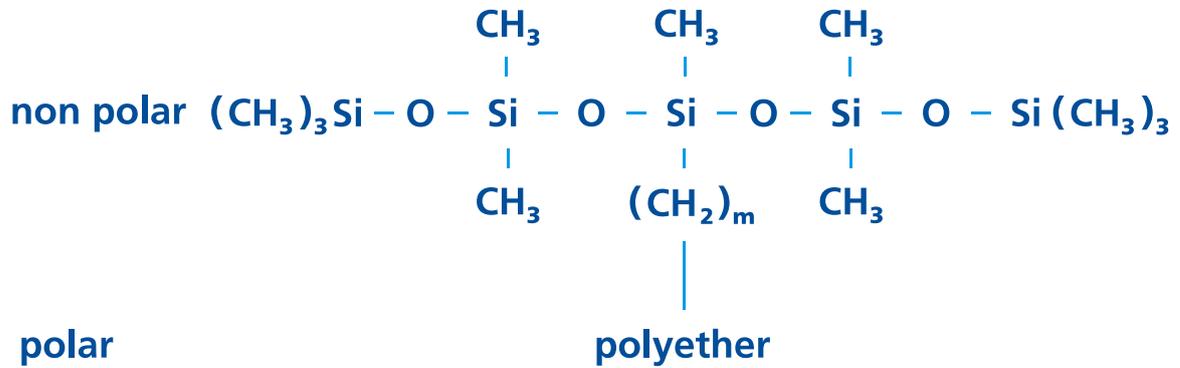
reactive group, e.g.

- OH
- acryl



Generally speaking, silicone additives are **non-reactive**, i.e. they do not interfere with the cross-linking reaction of the binder. For special applications, it can however be desirable for the silicone additive to be incorporated into the binder matrix. Reactive products have (at the terminal end of the organic modification) either primary hydroxyl groups (for reaction with isocyanates or other OH-reactive systems) or double bonds (for reaction with UV-curable systems).

Silicone surfactants



Silicone surfactants are polyether-modified dimethylsiloxanes, but in this case the molecular weights are considerably lower than the usual molecular weights of most other silicone additives. The siloxane chain consists of just a few Si-O units, and on average contains just around one polyether chain. For this reason, they have a quite pronounced **surfactant structure** (polar/non-polar). In aqueous systems, such products significantly lower the surface tension without simultaneously increasing the slip of the coating. If a greater slip is required, the silicone surfactants can easily be combined with other silicone additives which are suitable for aqueous systems.

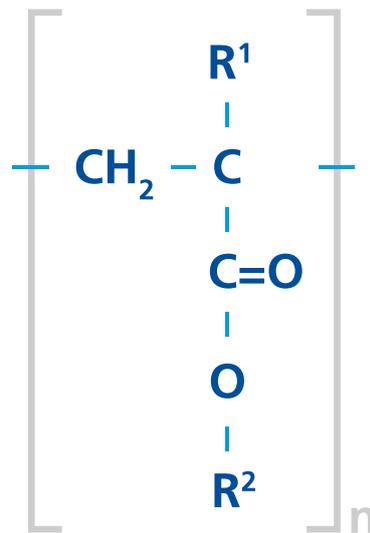
Compared with the fluorosurfactants, which are also frequently used when low surface tensions are required in coatings, the silicone surfactants have the advantage of not increasing the system's tendency to foam.

04

Chemical structure of polyacrylates

The basic components (monomers) of polyacrylates are **acrylic acid esters**. With the C=C double bonds, this molecule can be polymerized into long-chained polyacrylates. If, instead of acrylic acid esters, methacrylic acid esters are used, polymethacrylates are created.

Polyacrylates



$\text{R}^1 =$ -H: acrylat
-CH₃: methacrylat

$\text{R}^2 =$ alkyl, polyether,
polyester, amine salt



Usually, it is not acrylic acid itself that is polymerized, it is the acrylic acid ester, whereby in the monomers the hydrogen atom of the -COOH group is replaced by a different R-group. Possible modifications are: alkyl-, polyether- and polyester-chains. The acid group can also be neutralized with an amine. Reactive groups (e.g. OH) can also be incorporated into the side chains; such modified acrylate additives can be integrated into the coating film matrix during the cross-linking reaction of the binder. The molecular weight can be varied over a wide

range; the number of monomer units is typically between 40 and 800. Using just one type of monomer for the polymerization produces homopolymers, whereas co-polymers are created if several different types of monomers are used.

For **liquid coatings**, the polyacrylates are available either as a solvent-free additive (100 %) or in a diluted form (~50 %). For use in powder coatings, the polyacrylates are absorbed onto inert carriers (acrylate content ~60 %).

05

Methods of measuring surface tension

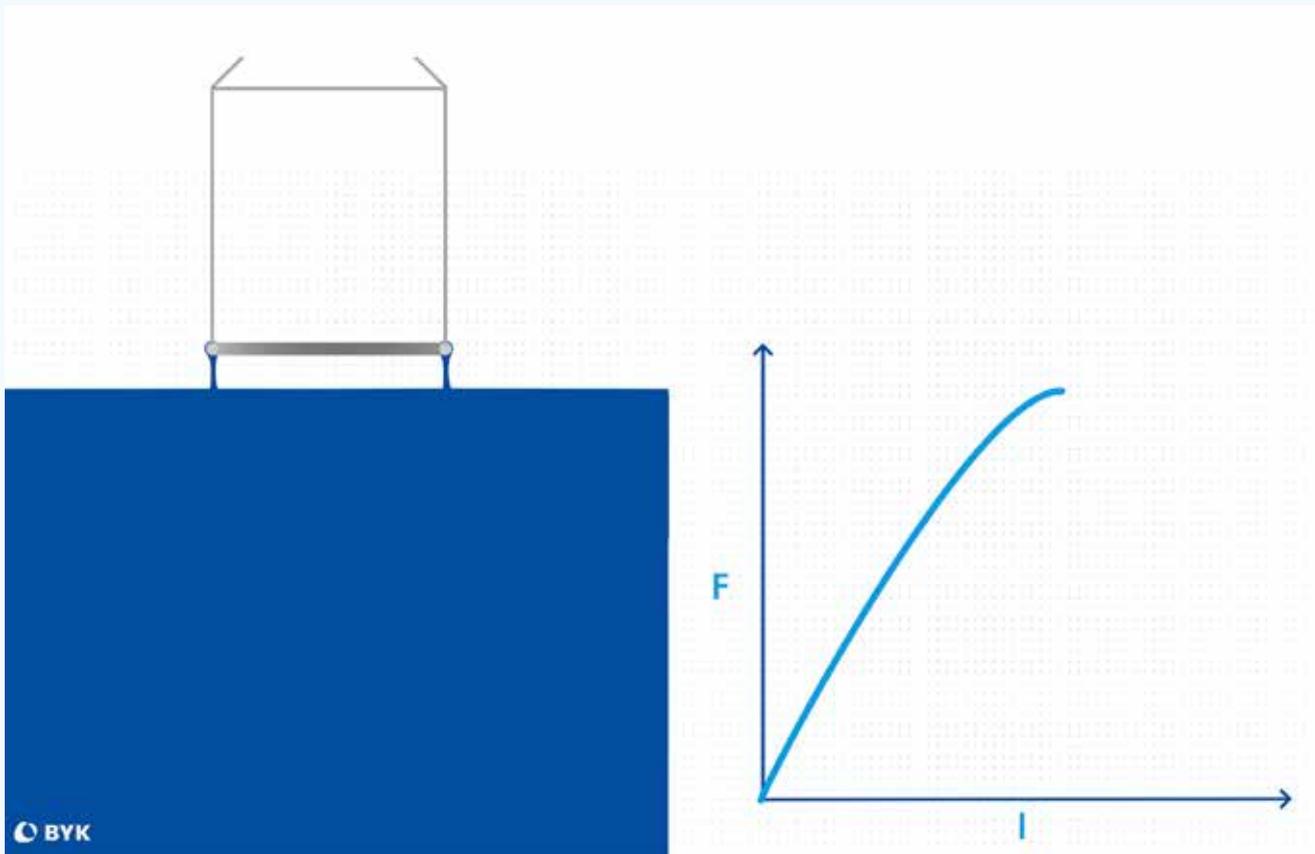
Static surface tension

The wetting of a surface with a liquid depends on the surface tension of the liquid. The definition of surface tension is the work that must be applied in order to enlarge the surface of a phase.

The Du Noüy ring method is used to determine the surface tension of a liquid. A platinum-iridium ring is drawn out of the liquid while, at the same time, the maximum force caused by the tension of the liquid lamella during the movement of the ring is measured.

$$\sigma_1 = \frac{F_{\max} - F_v}{L \cos \theta}$$

Du Noüy ring method



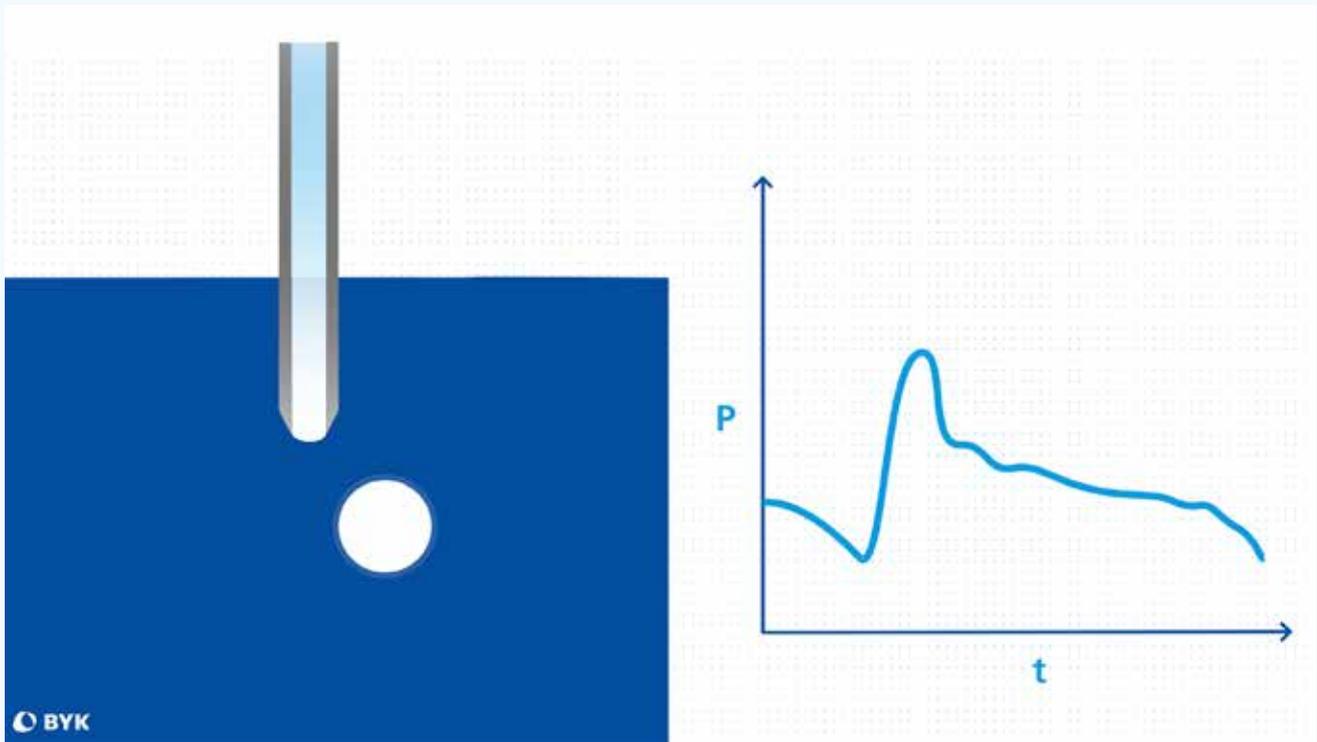
Dynamic surface tension

In fast application processes, the surface-active substances must be mobile in order to cover the newly created surfaces as quickly as possible and thereby keep the surface tension constant.

The bubble pressure method is used to determine the dynamic surface tension. Bubbles with different surface ages are generated within the liquid, and the maximum internal pressure of the bubbles is determined.

$$\sigma = \frac{1}{2} (P_{\max} - P_0) r_c$$

Bubble pressure method



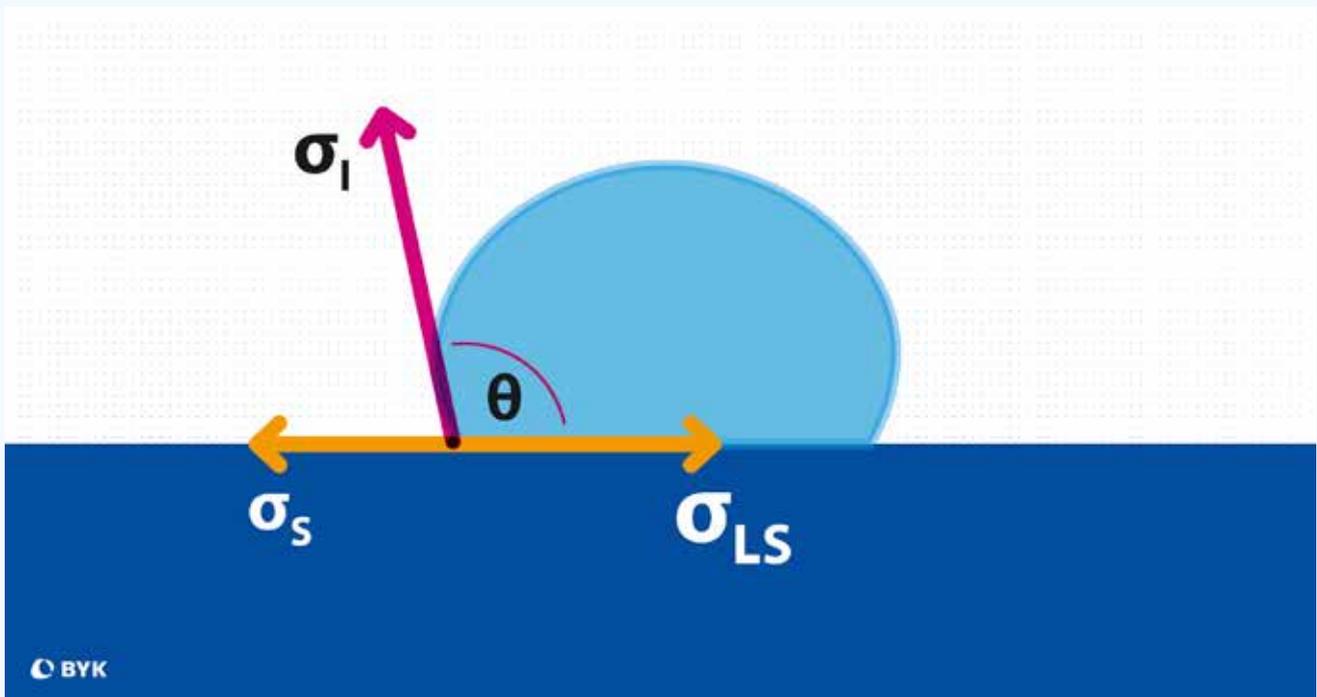
Contact angle measurement

The hydrophobic or hydrophilic properties of solids can be determined with the help of the contact angle measurement of water. To determine the free surface energy of solids, contact angle measurements are carried out with defined liquids, and these measurements are then used to calculate the free surface energy using different models (OWRK, Wu, etc.). In this way, the wetting behavior of liquids on these solids can be characterized.

$$\cos \theta = \frac{\sigma_s - \sigma_{ls}}{\sigma_l}$$

Young's equation

Contact angle measurement



06

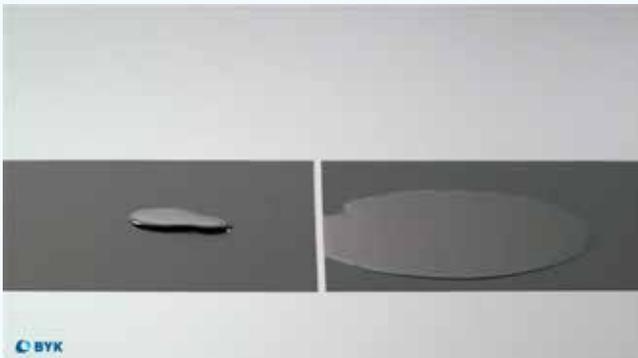
Substrate wetting

Substrate wetting

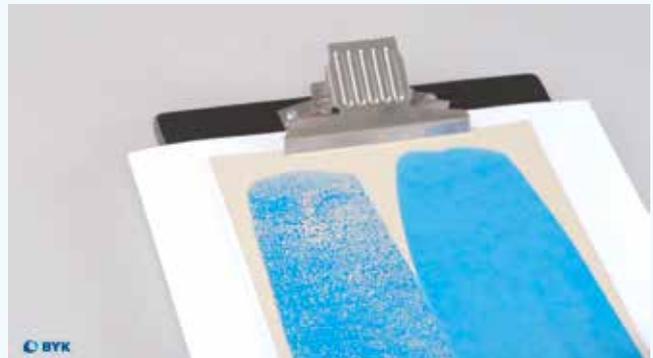
Substrate wetting primarily depends on the **surface tension of the liquid coating material** and the critical surface tension of the substrate to be coated. It is generally the case that the surface tension of the coating should be lower than or equal to the surface energy of the substrate in order to achieve a good wetting. Poor wetting, i.e. a crawling or beading of the coating will occur if the surface tension of the coating is higher than the surface energy of the substrate. Substrates with a generally **lower surface tension** (e.g. plastic parts) or contaminated surfaces (oil residue, release agent) are therefore difficult to wet.

Aqueous coating systems, due to their water content, have a higher surface tension than solvent-borne coatings, and therefore exhibit greater wetting problems. Silicone additives reduce the surface tension of the coating thereby resulting in a better wetting of the substrate. Silicones with dimethyl structures are preferable here, as these provide a rather **reduction of surface tension**. Especially for aqueous systems, silicone surfactants are also suitable. In addition, in aqueous systems, silicone-free surfactants based on alcohol alkoxyates can also be used as these also significantly lower the dynamic surface tension as well.

Additives based solely on polyacrylates are not suitable for improving substrate wetting.



Different reduction in the surface tension as a result of two different additive



Different wetting properties of a coating on leather (with and without additive)

07 Floating

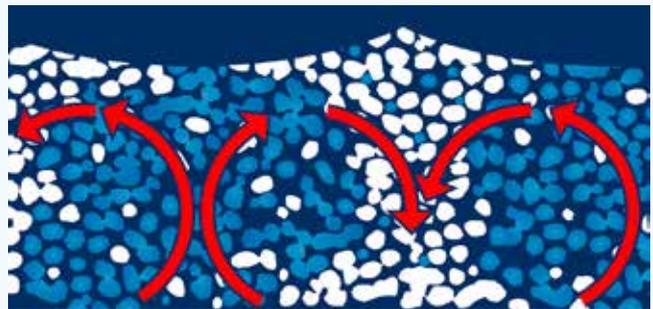
Floating, leveling problems, and air draft sensitivity

Solvents evaporating from a coating film cause **vortex flows** in the respective film. These arise because the more solvent-rich materials from the lower layers of the film must be continuously transported to the surface. This leads to the formation of a macroscopically visible cell structure (Bénard cells). Differences in density, temperature and, especially, surface tension are the driving forces of these movement processes. Various surface defects can ultimately result from these Bénard cells: floating, leveling problems, air draft sensitivity.

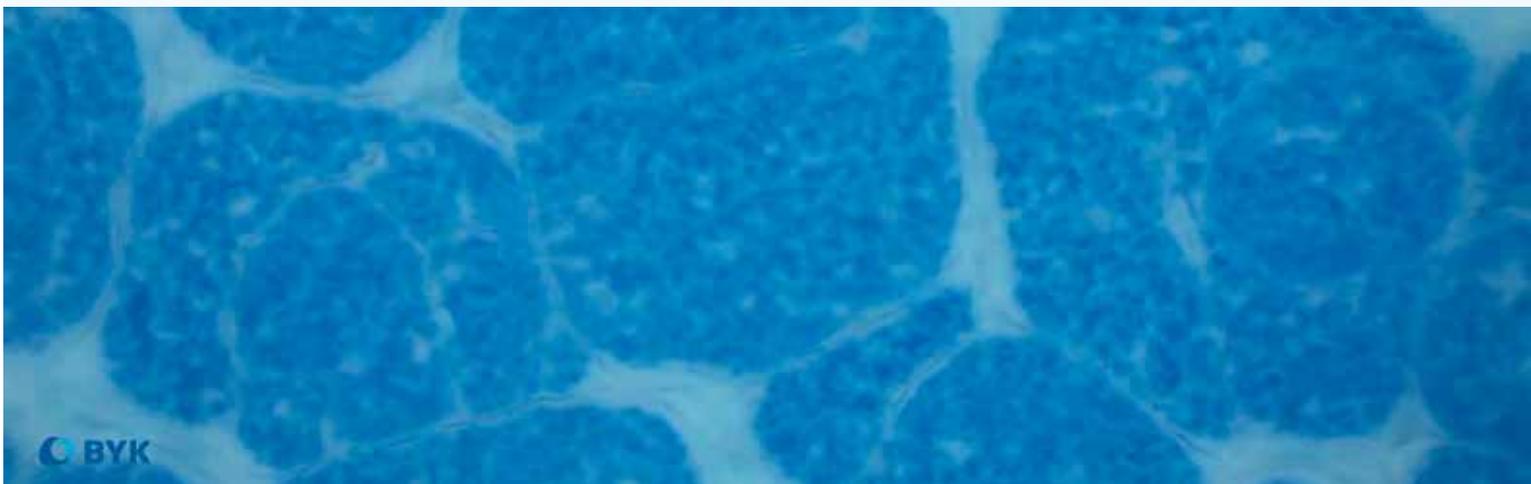
Floating

In a pigmented coating system, the pigments also participate in the vortex motion, and if the various pigments differ in their mobility, the flow processes can cause them to separate from one another. The pigments are then no longer homogeneously distributed within the coating surface (floating). On horizontal surfaces, the cell structure itself is visible; on vertical surfaces striation can be seen (silking).

Cross-section of Bénard cells:
separation of pigments
(floating)



Formation of Bénard cells in the liquid coating



08

Leveling

Leveling

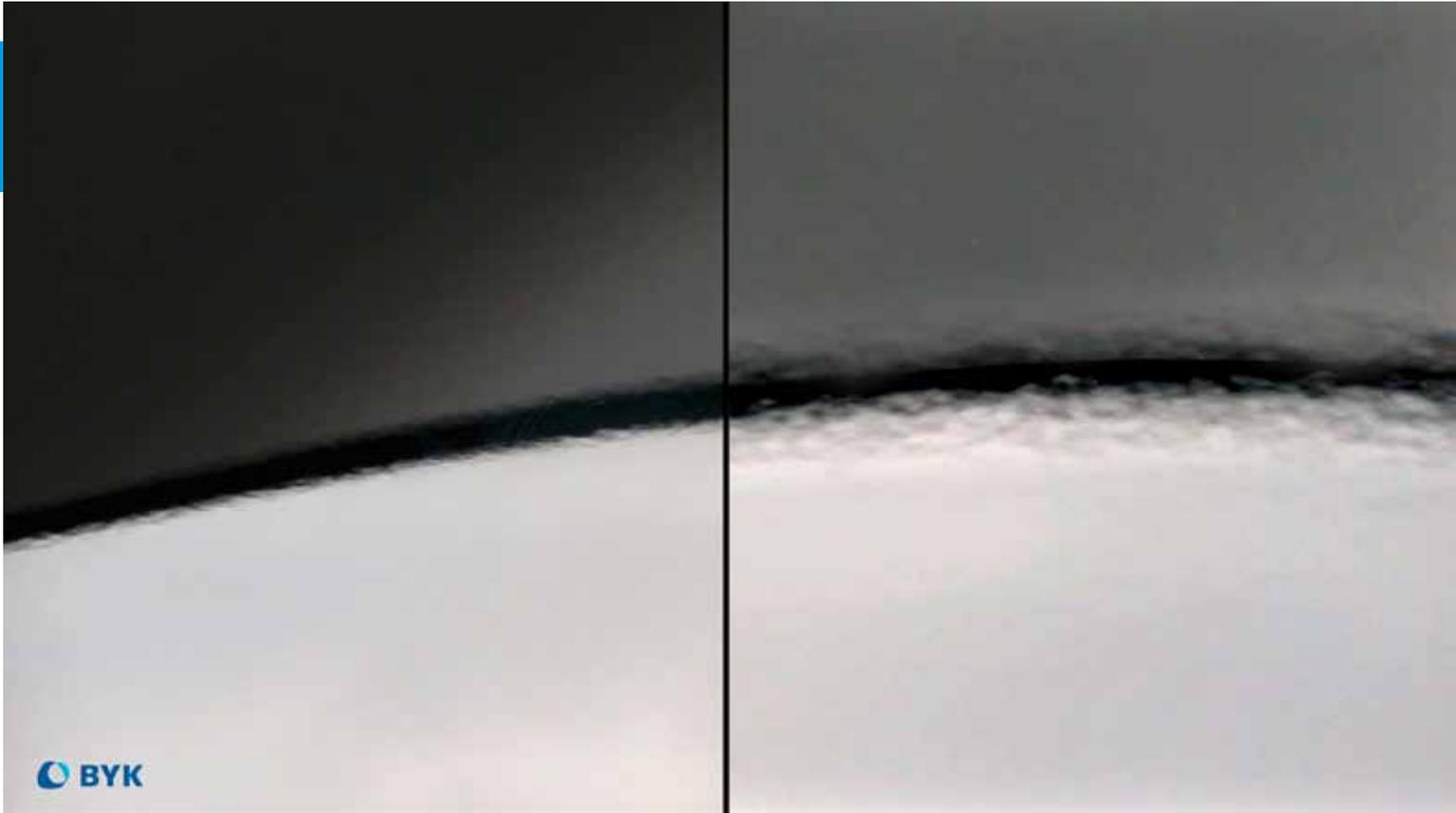
The formation of Bénard cells also leads, in many cases, to paint surfaces that are not uniformly smooth; rather, pronounced deformation or surface textures can occur. The coating exhibiting non-optimal flow will show varying degrees of a defect called "orange peel".

Air draft sensitivity

Depending on the drying conditions and the characteristics of the solvent mixture, the drying of the wet film or resin solution can occasionally become so strongly influenced by surface defects that the entire top surface of the film is completely disrupted. This extreme effect is called "air-draft sensitivity" and is generally caused by air-draft conditions that place extreme stress on the upper layers of the coating. It is an especially common occurrence in furniture coatings.

Leveling – surface flow control

During application	After application	
Surface flow control		
		
Typical example: low solids spray coating	Without leveling additive	With silicone leveling additive
Leveling		
		
Typical example: high-solids roller coating	Without leveling additive	With acrylate leveling additive



The wave-scan simulates visual observation. The wavy brightness pattern on the surface is optically scanned in the same way the human eye sees it. A laser point light source illuminates the sample at an angle of 60° ; a detector on the other side then measures the reflected light. The wave-scan device is moved over the sample across a defined range and measures the optical brightness profile from point to point.

The wave-scan analyzes the size of the structures: in order to take into consideration the resolution of the eye at different distances, mathematical filtering is used to divide the optical profile into long-wave (LW) and short-wave (SW) sections.

09

Preventing cratering

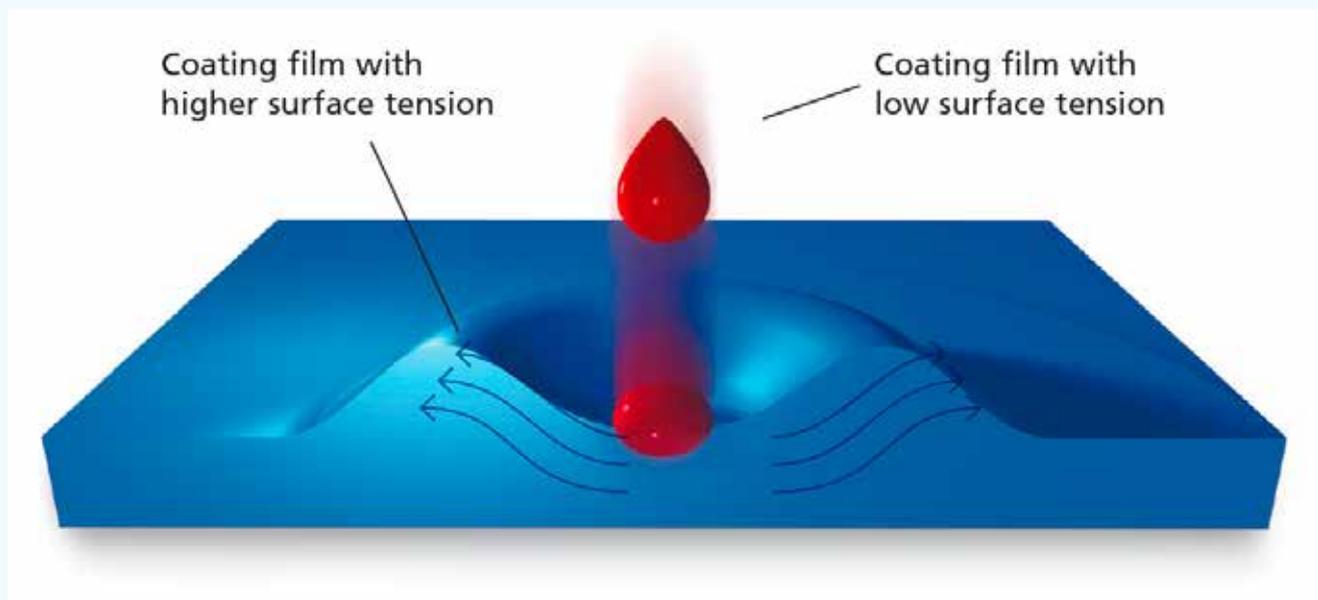
Prevention of cratering

The **causes** of cratering are diverse. Cratering can occur, for example, from overspray: if fine spray droplets of an overspray of a different coating material fall onto a freshly coated surface that is still liquid and mobile, these droplets can cause cratering if their surface tension is less than that of the surrounding coating film. Surface tension differences of 1-2 mN/m are already sufficient to cause spreading of the overspray droplets and, in consequence, cratering. If the surface tension of both materials is the same or if the spray mist has a greater surface tension, there are no spreading processes and therefore also no cratering. Small dust particles falling onto the liquid coating can provoke the same effect as overspray droplets. **Craters** can also be the result of a contaminated substrate (e.g. fingerprints or similar). If this contamination has a lower surface tension, it will cause cratering when the coating is applied. The occurrence of these effects is a special

case of a poor substrate wetting. By using a silicone additive, the **surface tension is lowered** and the coating is therefore much less susceptible to disturbances or disruptions, irrespective of whether they originate from the environment (overspray, dust particles, etc.), from the substrate (contamination), or even from the coating itself (gel particles). The coating process can be carried out more reliably through the use of silicone additives. In this case, when the greatest possible reduction in surface tension is needed, the use of silicone additives as anti-cratering agents is preferred.

Polyacrylates have barely any influence on the surface tension and are therefore ineffective as anti-cratering additives.

Cratering



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Surface slip

Surface slip

Silicone additives improve the surface **slip properties** of coatings. Often, however, it is not the slip itself but rather the addition of slip properties along with other features of a coating that are of prime interest. Obviously, surfaces with higher slip are more scratch resistant, less easily soiled, easier to clean, and more resistant to blocking. The level of improvement in the surface slip again depends on the chemical structure of the silicones and is directly linked to the proportion of dimethylsiloxane groups. Products with many dimethylsiloxane groups result in a **high surface slip**, while methyl alkyl polysiloxanes do not increase slip very much. Silicone surfactants, due to their small chain length, do not noticeably increase slip in the majority of coating systems. If more slip is nonetheless required, they must be combined with other silicone additives.



Measuring surface slip

Tape release

Good tape release properties are often required, especially in (but not limited to) the field of furniture coatings. This means that adhesive tape and labels can be removed from the coating easily and without leaving any residue. Silicone additives have an impact on this property. Specific additives are also provided with acrylic functions and can therefore be incorporated into the binder matrix in radiation-curable formulations.



Demonstration of increasing and reducing surface slip

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Cleanability

Improving cleanability

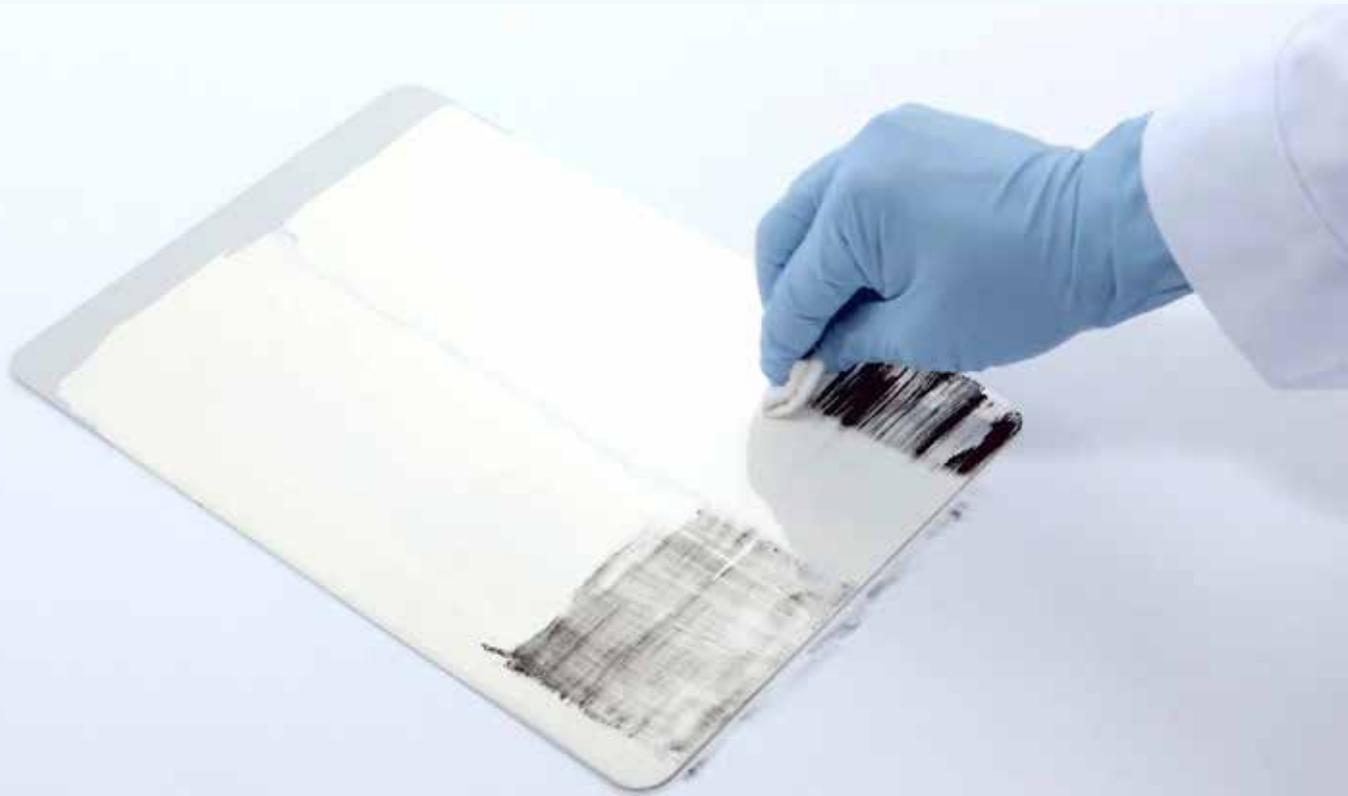
The use of special silicone additives also makes it possible to reduce the dirt pick-up of coatings and improve cleanability.

Such a special additive for solvent-borne coating systems is BYK-SILCLEAN 3700. It is a hydroxy-functional silicone-modified polyacrylate and, due to its surface activity, it migrates to the coating surface. Due to its primary OH groups, it can be incorporated into the polymer matrix in many coating formulations (e.g. 2-component polyurethane, alkyd melamine, polyester melamine, acrylate epoxy, epoxy phenol) during the cross-linking reaction. In this way the additive is permanently fixed at the coating's surface and the specific surface properties contributed by the silicone are also more permanent, including during outdoor exposure.

BYK-SILCLEAN 3700 makes coating surfaces simultaneously hydrophobic and oleophobic, which results in reduced dirt pick-up and improved cleanability. Water resistance is enhanced and whitening (blushing) avoided.

It can also be used to improve anti-graffiti and tape release properties. Moreover, BYK-SILCLEAN 3700 also improves substrate wetting, leveling and surface slip. For aqueous systems, the same properties can be achieved by using BYK-SILCLEAN 3720.

“Easy to clean” effect using BYK-SILCLEAN 3701



12

Practical information

Silicones as a general class of products have an unearned reputation in the industry for poor recoatability and intercoat adhesion. However, through proper choice and application, this does not have to be the case. Due to their surface activity, silicone additives migrate onto the coating surface and, as they usually have no reactive groups, they are not incorporated in the cross-linking mechanism of the binder, i.e. they remain mobile even after baking. This can be demonstrated, for example, by the fact that solvent can be used to wipe them off the surface again. When **recoating** a silicone-containing coating layer, the silicones then do not remain in the first layer (i.e. the interface between the two coating films); due to their mobility and surface activity they migrate to the new surface, i.e. that of the second coating film. No silicone remains between the two coating films, and for this reason the intercoat adhesion is not negatively influenced, either.

In connection with silicones, there are two factors, however, which can negatively influence intercoat adhesion:

(1) Dosage of the silicone additive,

(2) Baking temperature of the first coating.

For each binder/silicone combination there is an optimum quantity of silicone; higher dosages will not provide greater benefits (more wetting, anti-cratering effect, slip, etc.), but can cause undesirable side effects, such as impaired intercoat adhesion.

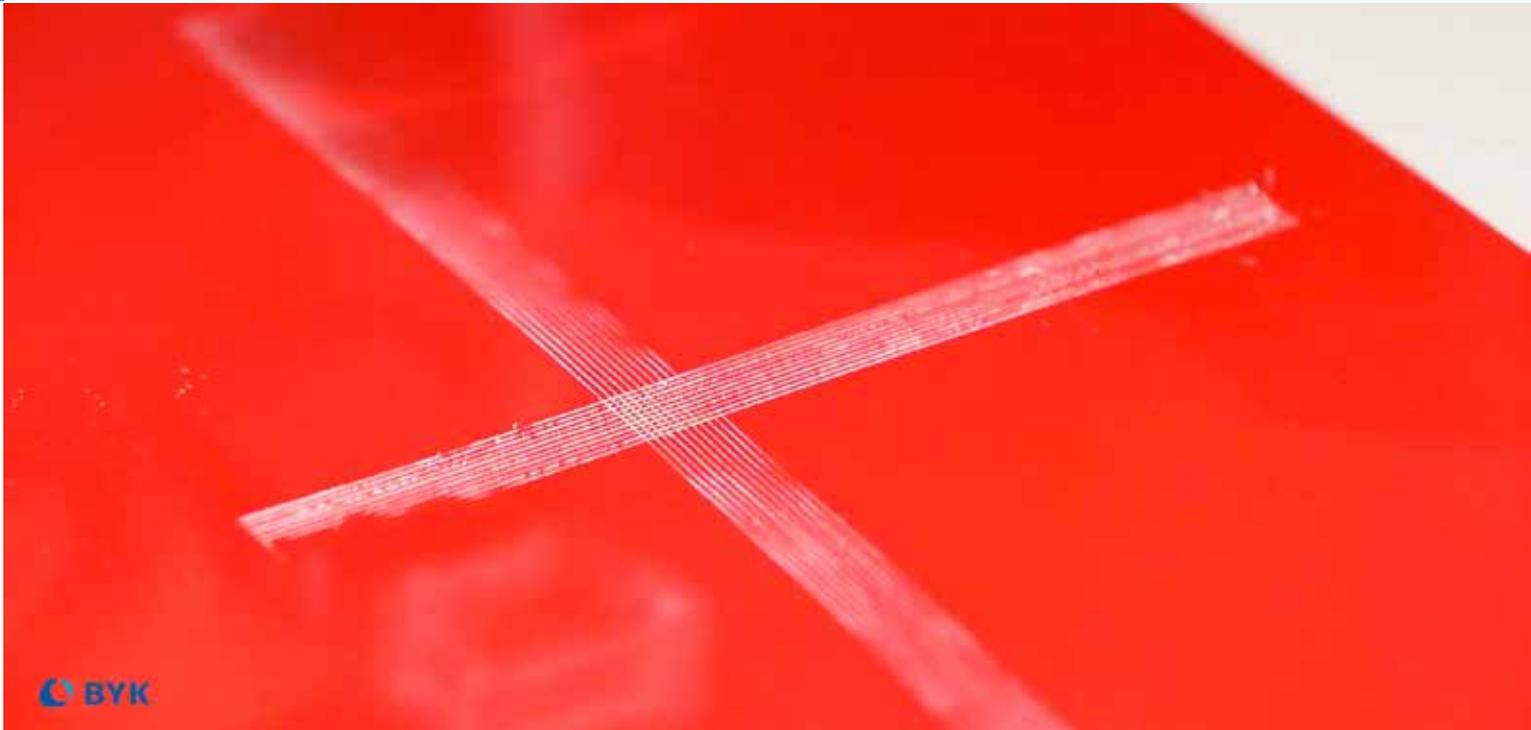
In the case of an **overdose**, some of the silicone molecules remain in the interface between the two coating films and adversely affect adhesion. When using silicones, it is therefore particularly important to use a series of tests to ascertain the optimum dosage and then not exceed it.

In addition, the baking temperature also has an influence on intercoat adhesion; when the first (silicone-containing) coating layer is **overbaked**, the adhesion of the second layer can be considerably reduced. This is due to the fact that at higher temperatures (140 °C-150 °C) the polyether chains of the additives are degraded by oxidation.

During these degradation processes, **reactive groups** are created, so that the silicone additive is now incorporated in the binder matrix and therefore loses its ability to migrate.

When overcoating, the decomposition products remaining between the two layers adversely affect adhesion by acting as a release layer. Since the thermal instability mentioned above is caused by the presence of polyether chains, it is therefore possible (by exchanging the polyether chains with more thermally stable groups) to avoid this effect. For example, silicone additives with polyester or aralkyl modifications remain stable at temperatures of up to 220 °C – 250 °C.

Intercoat adhesion can be assessed with the aid of cross-cut testing.



Defoaming

Foam can be caused by silicones, but silicones can also be used as **defoamers**. The critical factor here is the polarity and compatibility of the silicone additive. A highly compatible silicone additive with lower surface tension tends to stabilize foam. If this leads to problems with foam, products with a higher surface tension should be used instead. These products

are not defoamers, yet they contribute **defoaming properties** in addition to the typical silicone properties. Silicones which can be used as defoamers must be adjusted to become even more incompatible. Polyacrylates can also have a defoaming effect at a sufficiently high incompatibility



For more information on fields of application and products, visit our [BYK Additive Guide](#)