

Technical Information L-SI 1

# Surface Additives

# Surface Additives

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## Surface Defects – Causes and Prevention

Surface defects often occur during and after coating application. These defects degrade both the optical properties of the coating and its ability to protect the substrate. Typical defects are shown below:

- Poor substrate wetting (figure 1)
- Crater formation (figure 2)
- Formation of Bénard cells (figure 3) and flooding
- Non-optimal flow (orange peel) (figure 4)
- Air-Draft sensitivity.

One very significant parameter affecting all these defects is the **surface tension** of the involved materials. More specifically, surface tension differences are the actual cause of these surface defects. The source of surface tension differences can be within the system itself (solvent evaporation or the crosslinking reaction of the resin) or external sources; (overspray, dust particles, or contamination of the substrate).

To prevent surface tension defects, additives may be used. They modify the surface tension of the paint and/or minimize surface tension differences. Basically, the composition of these products are polysiloxanes or polyacrylates. If considerable surface tension differences must be equalized, polysiloxanes can be used. They will – depending on their chemical structure – strongly reduce the surface tension of the liquid paint. They can be used for improving the substrate wetting and as anticratering additives. If they are sufficiently incompatible with the paint system, these polysiloxanes also exhibit defoaming properties.

Silicone additives can also be used to improve the surface slip of the dried or cured paint film, as well as improving 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 paint. They are mainly used for flow improvement. In case of sufficient incompatibility, these products can also exhibit defoaming properties.

In addition to **polysiloxanes** and **polyacrylates**, low molecular weight surfactants are also available. Due to their typical surfactant structure (polar/non-polar segments) they are surface active and can be used to reduce surface tensions.

### Insufficient Substrate Wetting



figure 1

### Craters

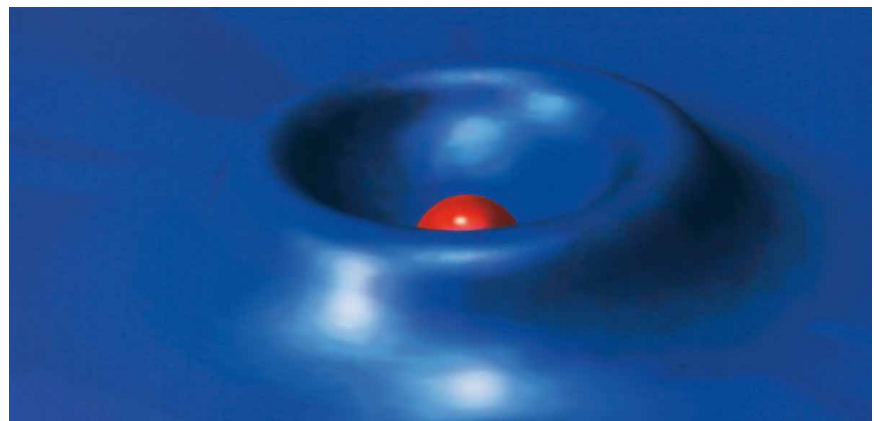


figure 2

### Bénard Cells

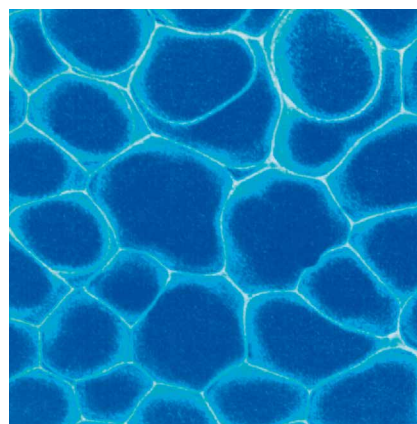


figure 3

### Insufficient Flow

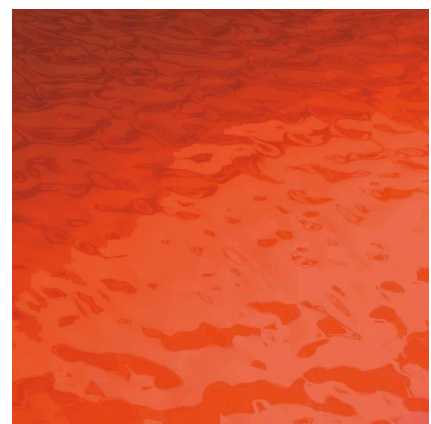


figure 4

## Chemical Building Blocks of Polysiloxanes

### Polydimethylsiloxane

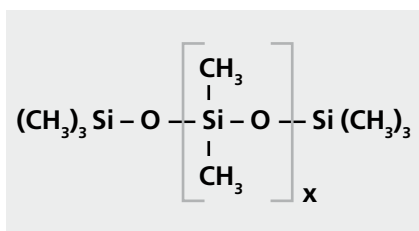


figure 5

“Silicone additives” (also abbreviated “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 fashion, one can readily learn how to overview and characterize silicone additives. Additionally, the correlation between structural features and resultant properties will become more understandable.

### Polydimethylsiloxanes

All silicone additives are derived from the basic structure of polydimethylsiloxane (figure 5).

Through variations in chain length, a variety of different products with great differences in properties and features are available. Short-chain silicone additives are relatively **compatible** in paint systems. Typical silicone properties (such as low surface tension, improved flow, etc.) are exhibited. Higher molecular weight, long-chain molecules are rather **incompatible** and can potentially lead to cratering and hammertone effects. Accordingly, pure polydimethylsiloxanes (silicone oils) are rarely ever used in modern paints.

### Polyether modified Polydimethylsiloxane

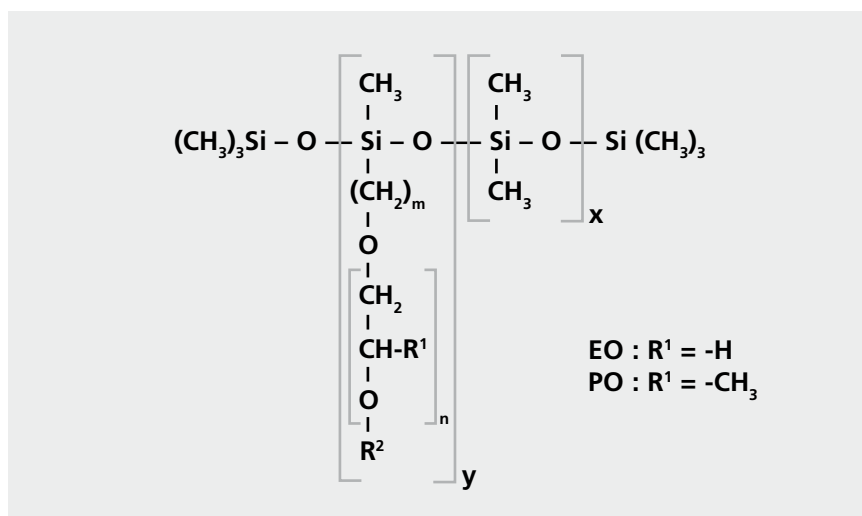


figure 6

### Polyether Modification

A more elegant method than chain-length-dependent compatibility is to modify the silicone backbone structure through the introduction of sidechains. Most silicone additives today are **“organically modified polysiloxanes”**. In most cases, the most important feature is the modification with **polyether** side-chains (figure 6). Through the introduction of various types and number of side-chains, compatibility can be improved or modified. The relationship or proportion of dimethyl groups to polyether modification (x to y) allows the chemist to control the degree of compatibility. Simultaneously, this also can influence **surface tension**; (for example, the more dimethyl groups available, the lower the surface tension, as a rule of thumb). Furthermore, the structure of the polyether chains themselves can be varied. An important factor here is the **polarity** of the structural elements. The polyether chain itself is composed of ethylene oxide (EO) and/or propylene oxide (PO) units. Polyethylene oxide is very hydrophilic (polar); whereas, polypropylene oxide by comparison, is rather hydrophobic (nonpolar).

By varying the proportions of EO to PO, the polarity of the entire silicone additive can be controlled or modified.

For example, a higher proportion of EO raises the polarity so the additive is more water soluble and therefore more compatible in higher polarity paint systems. However, the tendency for foam stabilization increases; a higher proportion of propylene oxide (PO) will reduce both water solubility and foaming tendencies.

### Polymethylalkylsiloxanes

Another possibility for modifying the silicone structure is to replace one of the methyl groups of the dimethyl structures (either partly or entirely) with a long-chain alkyl group. Polymethylalkylsiloxanes (figure 7) are the result. In comparison to polydimethylsiloxanes, such products clearly demonstrate higher surface tension, and exhibit less influence on surface slip. They are often the active constituents in defoamers (e.g.: BYK-077).

Polymethylalkylsiloxanes can be organically modified with polyether chains in the same manner as polydimethylsiloxanes. Along with their well known silicone properties, they also exhibit slight defoaming properties.

### Other Types of Modification

Polyether modified polysiloxanes are thermally stable up to about 150°C/300°F. At higher temperatures, the polyether chains will decompose. Through the use of non-polyether structural elements such as polyester and aralkyl groups (figure 8), various thermally stable products can be produced. These modified polysiloxanes are thermally stable up to 220°C/430°F and can be used at much higher oven and cure temperatures. >

### Polymethylalkylsiloxane

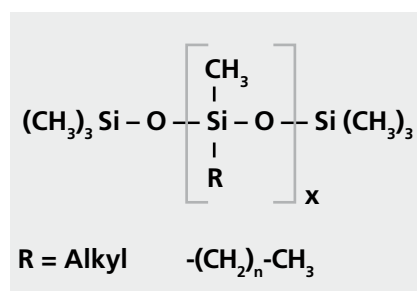


figure 7

### Thermostable modified Polysiloxane

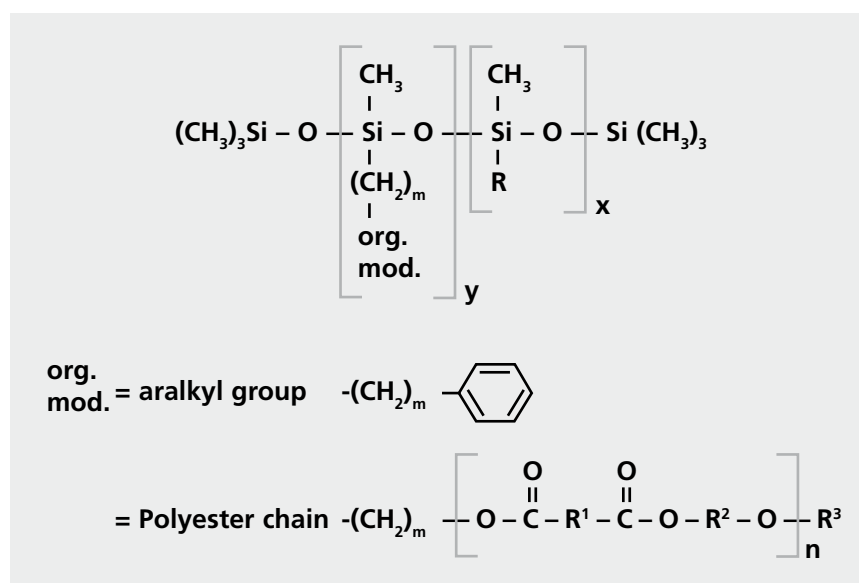


figure 8

## › Chemical Building Blocks of Polysiloxanes

### Reactive Silicones

As a rule, silicone additives are not reactive; typically, this means that they do not take part in the crosslinking reaction of the resin itself. However, for special applications, it may be desirable for the silicone additive itself to be incorporated into the binder structure. For such situations, reactive silicone additives with special functional end "group" structures are available. 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

Chemically speaking, silicone surfactants are polyether modified dimethylsiloxanes. However, in this case, their molecular weights are considerably lower than the usual molecular weights of most other silicone additives. The silicone chain consists of only a few Si-O units and, on average, one polyether chain. For this reason, these products have a very pronounced surfactant structure (polar/non-polar) and in aqueous systems significantly lower the surface tension without increasing the slip properties of the coating. If high slip is required, silicone surfactants can be combined with other silicone additives suitable for aqueous systems.

### Reactive Silicones

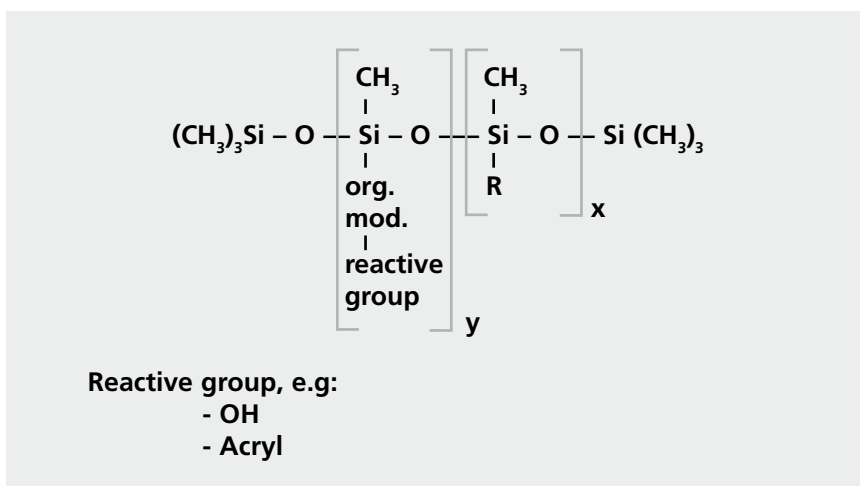


figure 9

### Silicone Surfactant

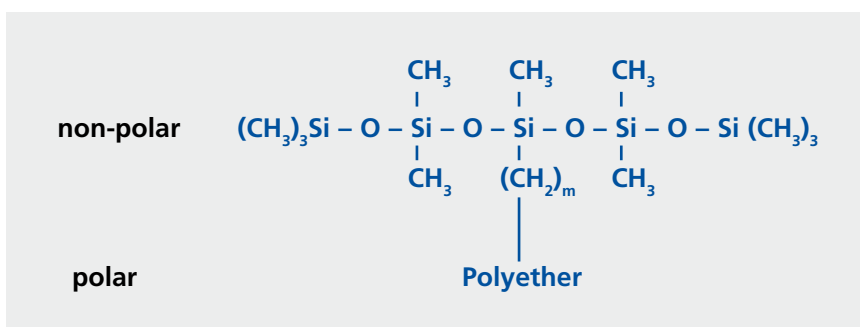


figure 10

## Chemical Building Blocks of Polyacrylates

**Acrylic acid** is the basic component (monomer) of polyacrylates.

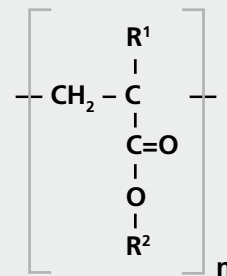
The C=C double bond site of this molecule can be polymerized to give long-chain polyacrylic acids. If methacrylic acid is used as a monomer instead of acrylic acid, then the corresponding polymethacrylates are formed.

Typically, the ester of the acrylic acid is used, rather than the acrylic acid itself. The hydrogen atom of the COOH-group in the monomeric acrylic acid is replaced by another group. Possible modifications are alkyl-, polyether- and polyester-chains. The acid group can also be neutralized by amines. Reactive groups (e.g. -OH) can also be built into side-chains. Acrylate additives modified in this manner, can be integrated into the paint film matrix during the crosslinking reaction of the binders. The acrylate's molecular weight can be varied within a wide range, typically between 40 and 800. If a single monomer is used for polymerization, homopolymers result. If there are several monomers, copolymers result.

For liquid paints, polyacrylate additives are available in either solvent-free (100%) or diluted form (~50%).

For powder coatings, polyacrylates are adsorbed onto inert carrier substrates (acrylate content ~60%).

### Polyacrylates



**R<sup>1</sup> = -H: Acrylate**  
**-CH<sub>3</sub>: Methacrylate**

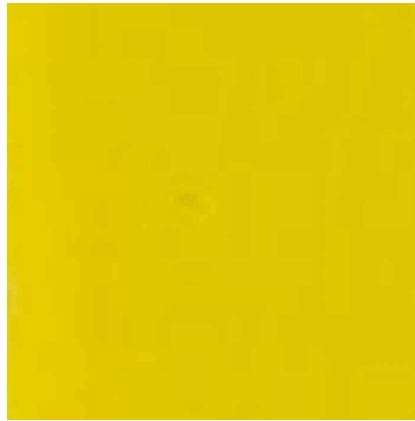
**R<sup>2</sup> = Alkyl, polyether, polyester, salt**

figure 11

Substrate Wetting – I



Poor substrate wetting on oily substrate



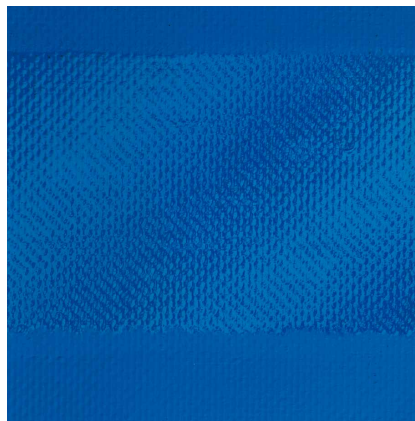
Good Wetting by Using a Surface Additive

figure 13

Substrate Wetting – II



Poor substrate wetting of an aqueous coating on PVC foil



Good Wetting by Using a Surface Additive

figure 14

## Uses for Surface Additives

### Substrate Wetting

Substrate wetting depends primarily on the surface tension of the paint and the critical surface tension of the substrate to be coated. As a general rule, the surface tension of the paint must be lower than or at least equal to the surface tension of the substrate. Poor wetting (such as “crawling” or beading of the paint) will occur when the surface tension of the paint is greater than the surface tension of the substrate.

Substrates with low surface tensions (for example plastics, or substrates with residue of oil or contamination) are therefore not easily wetted. Waterbased paint systems, because of their water content, are obviously higher in surface tension than paint systems with organic solvents, and exhibit, in many cases, problems with substrate wetting. Silicon additives reduce the surface tension of the coating, thereby resulting in better substrate wetting. By way of preference, silicones with dimethyl structures are used because these particularly **strongly reduce** the **surface tension**.

Silicone surfactants are also highly suited to aqueous systems. Silicone-free **surfactants** based on alcohol alkoxylates can also be used in aqueous systems as these also significantly lower the dynamic surface tension.

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



**Bénard Cells, Flooding & Floating, Flow, Air-draft Sensitivity**

During the processes of dry and cure, turbulent flow patterns often arise in the wet film. Such turbulence is constant in nature, and transports material from the lower layers of the film to the surface of the film. This leads to the formation of macroscopically visible cell structures (Bénard cells). Differences in density, temperature, and especially surface tension are the driving force behind this cell formation process. Many different surface defects can be traced to Bénard cells: flooding & floating, flow, and air-draft sensitivity.

**Flooding & Floating:**

In pigment-containing paint systems, the pigments themselves will take part in the circular flow patterns. In cases where different pigments with correspondingly different mobilities interact, these pigments can become widely separated through these flows and disturbances in the film. On the paint surface, pigments will no longer be homogeneously distributed. On horizontal surfaces, Bénard cells will be seen as a float; on vertical surfaces as silking.

**Flow:**

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 exhibit 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. >

**Bénard Cells – Top View**

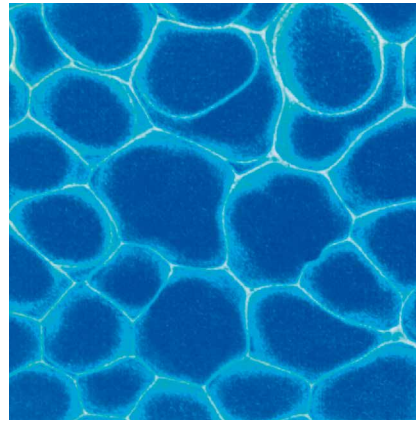


figure 15

**Bénard Cells – Cross Section: Pigment Separation (Flooding & Floating)**

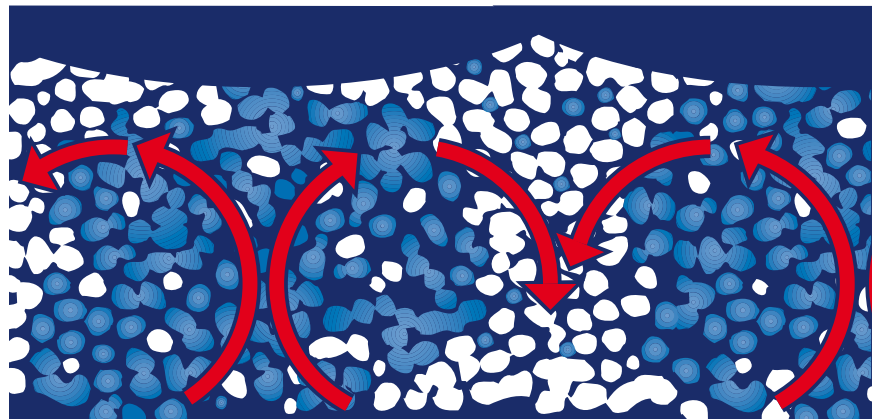


figure 16

**Surface Flow Control – Leveling**

During application	After application	
<b>Surface flow control</b>		
Typical example: Low solids spray-applied finish	Without surface flow control additive	With surface flow control additive (silicone)
<b>Leveling</b>		
Typical example: Roller-applied high solids finish	Without leveling additive	With leveling additive (acrylate)

figure 17

## › Uses for Surface Additives

### Problems solved with Silicone Additives

Through the use of silicone additives, the surface tension of the paint can be stabilized at a relatively low value and surface tension differences therefore, cannot develop. Since surface tension differences are integrally connected with the formation of cell structures, the subsequent elimination of surface tension differences prevents the formation of many undesirable defects. Almost all silicone additives can be used to prevent Bénard cells. However, in the case of flooding the silicone influences only the cell structure itself rather than the underlying cause (namely, different pigment mobilities). Specialized wetting and dispersing additives can be used to control such pigment mobilities, thereby allowing the silicone additive to function in a supporting role. Through the introduction of silicone additives as surface flow control (SFC) additives surface properties can be controlled. For example, low surface tension leads to short wave structures at the surface of the film; while high surface tension leads to comparatively long wave structures. However, in terms of improving leveling, polyacrylates are far more important than polysiloxanes (see following section).

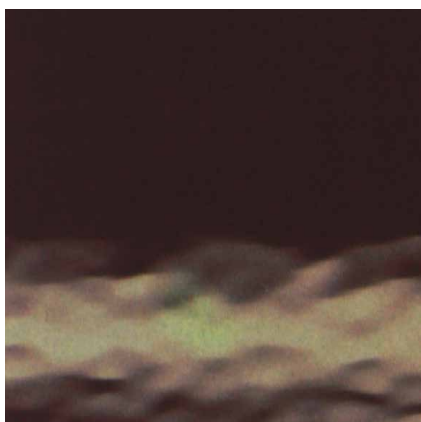
### Problems solved with Acrylate Additives

Polyacrylate additives are used first and foremost when leveling needs to be improved. They are available in graduated polarities to achieve optimal leveling in the most diverse coating systems. Acrylate additives with a high molecular weight are significantly less compatible and therefore also have a degassing effect. In addition to surface tension, the rheology of the coating is crucial to leveling behavior: the flow properties are considerably influenced both by specialist rheology additives and also by wetting and dispersing additives. Leveling problems can therefore often be resolved without leveling additives, taking into account the other formulation components. For **powder coating applications** there are also acrylate leveling additives in powdered form. Polyacrylates in these cases are adsorbed on to a porous, siliceous carrier material.

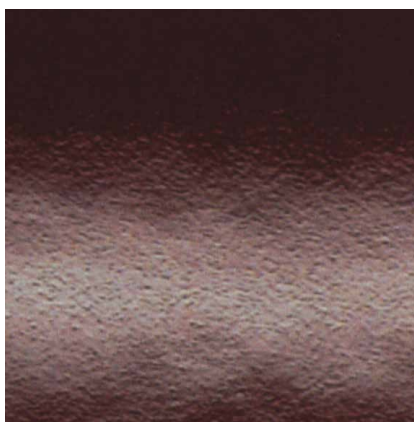
### Silicone/acrylate-combinations

In practice, to get the best paint surface properties, a combination of polysiloxanes and polyacrylates is often recommended. Through their strong surface activity, the silicone additives give crater-free surfaces and good substrate wetting, while the acrylate additives optimizes leveling.

### Surface Defects



Long wave



Short wave

figure 18

### Anti-cratering

The causes for crater formation can be very diverse. Craters can be caused, for example, by overspray falling onto a freshly sprayed paint film that is still mobile. Fine spray droplets of overspray will lead to craters if the surface tension of the droplets is lower than the surface tension of the wet paint surface. Surface tension differences of 1-2 mN/m (Dynes/cm) are enough to cause spreading of the droplets, leading to craters. In cases where the surface tension of both materials are the same, or if the overspray has higher surface tension; then there is no spreading of the droplets and consequently, no crater formation. Small dust particles falling onto the wet paint layer can have the same effect as overspray droplets. Craters can also originate from uncleaned or contaminated substrates (for example, fingerprints). When the contaminations are low in surface tension, they can lead to craters when the paint is applied. The occurrence of these defects are a special case of improper substrate wetting. Through proper utilization of silicone additives, surface tension is lowered, the paint becomes visibly less susceptible to disturbances or disruptions from the environment (overspray, dust particles, etc.), from the substrate (contamination), or even from the coating itself (gelled particles). Through the use of silicone additives, the application properties of the coating becomes more forgiving. In this case, when the greatest possible reduction in surface tension is achieved, it is preferable to use polydimethylsiloxanes as anti-cratering additives. Polyacrylates have only slight influence on surface tension, and therefore do not work as anti-cratering additives.

### Craters

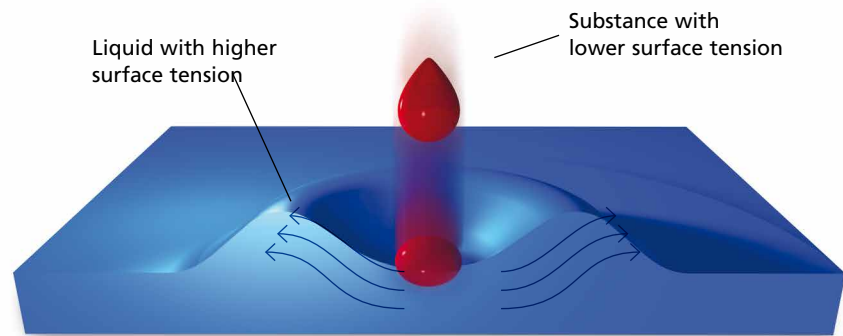


figure 19

### Defoaming

Although foam can be caused by silicones, silicones can also be used as **defoamers**. The critical factor here is the polarity and compatibility of the silicone additive. Highly compatible silicone additives with low surface tension tend to stabilize foam. If this causes foam problems, products with a higher surface tension should be used. These products are not defoamers, yet they contribute **defoaming properties** in addition to the typical silicone properties. Silicones that can be used as defoamers need to be adjusted to become even more incompatible. Polyacrylates can also have a defoaming effect at a sufficiently high incompatibility. >

## › Uses for Surface Additives

### Tape Release



figure 21

### Surface Slip

Silicone additives can be used to improve the surface slip properties of coating. Oftentimes, it is not mere 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 degree of surface slip improvement is dependent primarily upon the chemical structure of the silicone and, in particular, on the proportion of dimethyl groups present. Products with many dimethyl groups provide higher slip, whereas methylalkylpolysiloxanes provide markedly less improvement in slip. Silicone surfactants, due to their short chain lengths will not provide surface slip in most paint systems. If surface slip is desired, additional silicone additives must be used along with the silicone surfactants.

### Tape Release

Furniture coatings are one application but not the only one where good tape release is a frequent requirement. This refers to a property whereby 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-curing formulations.

### Improving the Ease of Surface Cleaning

Special silicone additives are available to reduce dirt pick-up and improve the surface cleaning properties of paint surfaces.

BYK-SILCLEAN 3700 is such a specialized product for solvent-borne coatings. It is a hydroxy functional silicone-modified polyacrylate and migrates to the coating surface due to its surface activity. In many coating formulations, (e.g. 2-pack polyurethanes, alkyd-melamines, polyester-melamines, acrylate-melamines, acrylate-epoxies, epoxy-phenols) the additive can be crosslinked into the binder network via its primary hydroxyl groups. In this way the additive is permanently fixed at the coating's surface and the specific surface properties contributed by the silicone are then also more permanent, including during outdoor exposure.

BYK-SILCLEAN 3700 renders the surface of the coating to be both hydrophobic and oleophobic, which explains the reduced dirt pick-up and improved ease of cleaning. Water resistance is enhanced and whitening (blushing) avoided. This additive can also be used to enhance anti-graffiti and tape-release properties. In addition to these specific features, BYK-SILCLEAN 3700 also improves substrate wetting, leveling and surface slip. In aqueous systems the same properties can be achieved with BYK-SILCLEAN 3720.

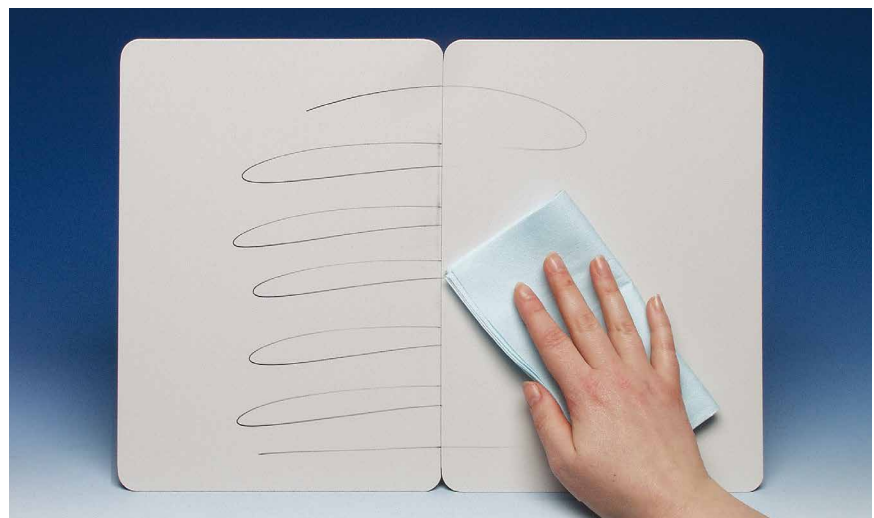
### Easy Surface Cleaning



The coating of the panel on the right side contains BYK-SILCLEAN 3700. The surface is contaminated with red iron oxide pigment and then rinsed with water. The contamination is easily removed on the right panel (with additive) but not on the left panel (no additive).

figure 22

### Easy Surface Cleaning



Again the coating on the panel on the right side contains BYK-SILCLEAN 3700. Felt tip marking pens show poor wetting and adhesion on this surface and can be removed easily.

figure 23

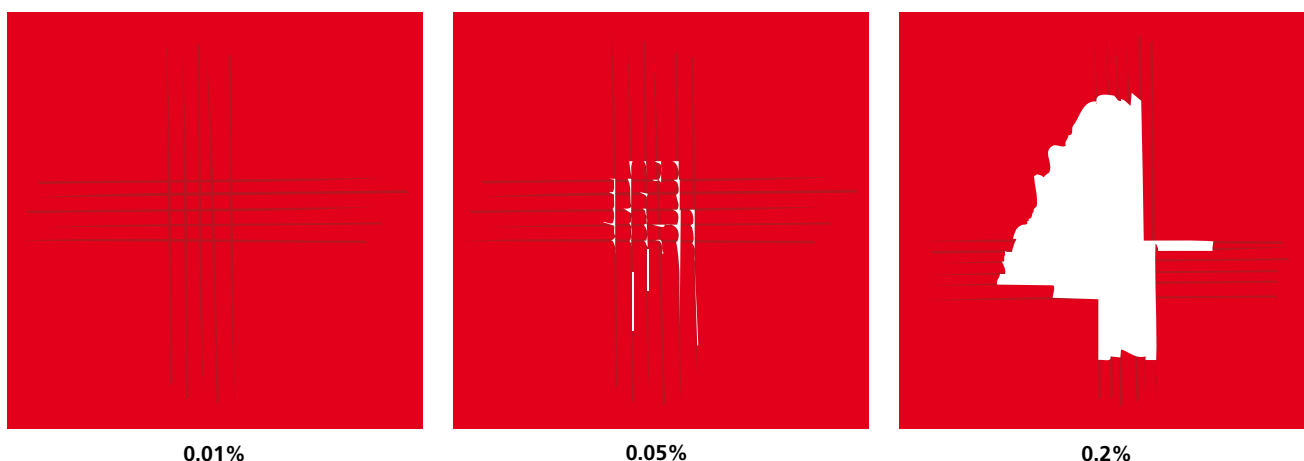
## Silicone Additives and their Influence on Intercoat Adhesion

Silicones as a general class of products have an unearned reputation in the industry for being unrecoatable and degrading intercoat adhesion. However, through **proper choice** and application, this does not have to be the case. Silicone additives migrate to paint surfaces because of their surface activity. Since they, as a rule, have no reactive groups, they do not participate in the drying/curing mechanism of the binder. In other words, this means that silicones will remain mobile throughout the entire curing process. This can be demonstrated by the fact that the additive can be removed by wiping or solvent rinse.

During the process of **overcoating** the initial silicone containing layer, the silicones do not remain static at the surface of the first layer (namely the interfacial layer between the two paint films), but rather migrate because of their mobility and surface activity, to the new surface of the second paint layer. No silicone remains between the two layers of coating. There is therefore no loss of intercoat adhesion. However, there are at least two conditions that can influence intercoat adhesion:

(1) the **amount** of silicone additive, and (2) the **curing temperature** of the first paint film. For every resin/silicone combination there is an optimal silicone level. Higher levels do not provide additional advantages (wetting, anticrater effect, slip, etc.) but may cause undesirable side effects such as loss of intercoat adhesion. Through **overdose**, some silicone molecules will remain in the interfacial layer between the two paint films and adversely affect adhesion. This means that it is very important to adjust the level of silicone so that it is optimal.

### Influence of Silicone Dosage

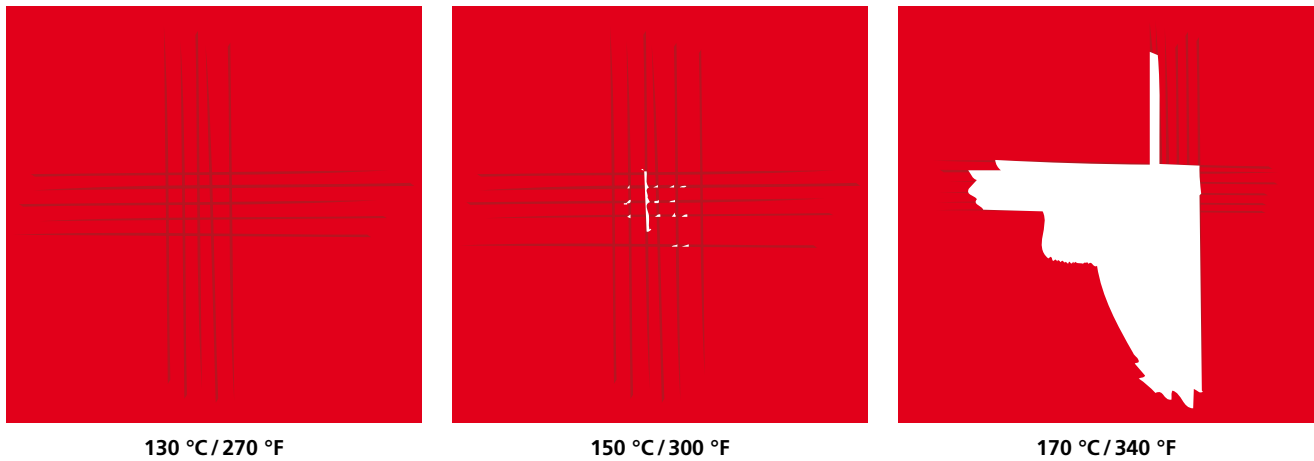


The first (white) layer of paint is applied and contains the stated amount of silicone additive (active substance on total formulation). After baking, the second (red) layer is applied and baked as well. Then a cross-cut test is performed and adhesion properties are judged by means of adhesive tape lift-off. Poor adhesion in case of silicone overdosage is very obvious. The limiting silicone concentration is dependent on the silicone additive and the resin system; the values given here are just for illustration.

figure 24



## Influence of Baking Temperature



The first (white) paint layer contains a polyether modified silicone and is baked for 30 minutes at the stated temperatures. Afterwards, the second (red) layer of paint is applied and baked at 130 °C in all cases. Then a cross cut-test is performed and adhesion properties are judged by means of adhesive tape lift-off. Poor adhesion in case of overbaking the first paint film is very obvious. The critical baking temperature varies with the type and dosage of the silicone additive and the resins used; the values given here are just for illustration.

figure 25

One method of determining optimal use level is to use "ladder studies" in which the exact quantity of additive is adjusted to maximize the resin and paint system attributes. In addition to proper level, baking temperature can also influence intercoat adhesion. In systems where the proper baking temperature of the first coating layer (containing silicone) is exceeded, the intercoat adhesion between first and second layer can be reduced. This is because the polyether chains of the additives are oxidized at higher temperatures (140 °C – 150 °C / 280 °F – 300 °F). Through this oxidation process, **reactive groups** are created in the additive so that the silicone additive now becomes an integral part of the coating system 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 / 430 °F – 480 °F.

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Additives:

**BYK-Chemie GmbH**  
P.O. Box 100245  
46462 Wesel  
Germany  
Tel +49 281 670-0  
Fax +49 281 65735

[info@byk.com](mailto:info@byk.com)

Instruments:

**BYK-Gardner GmbH**  
P.O. Box 970  
82534 Geretsried  
Germany  
Tel +49 8171 3493-0  
+49 800 427-3637  
Fax +49 8171 3493-140

[info.byk.gardner@altana.com](mailto:info.byk.gardner@altana.com)



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