

Substance for Success.



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

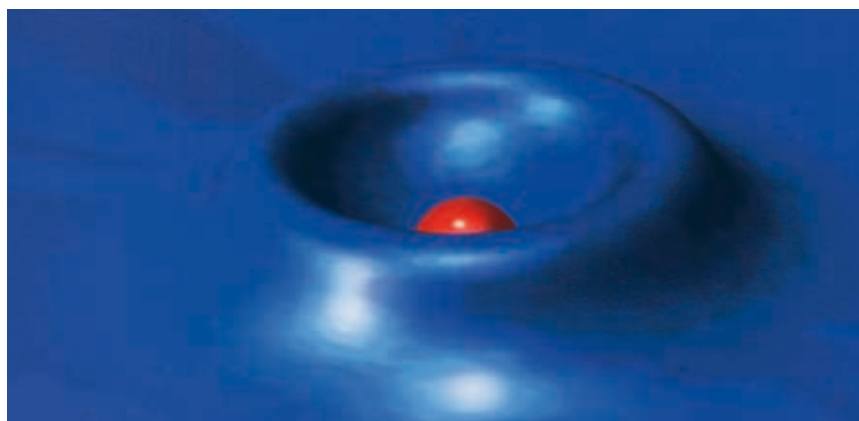


figure 2

Bénard Cells

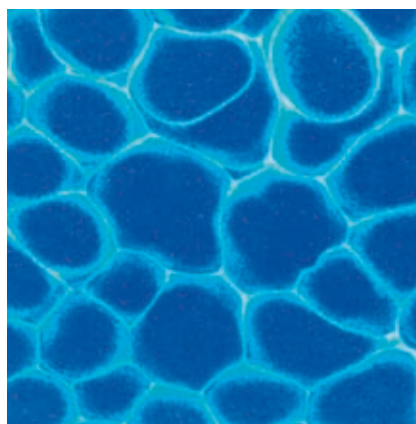


figure 3

Insufficient Flow



figure 4

Chemical Building Blocks of Polysiloxanes

Polydimethylsiloxane

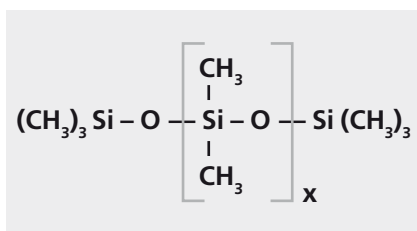


figure 5

“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

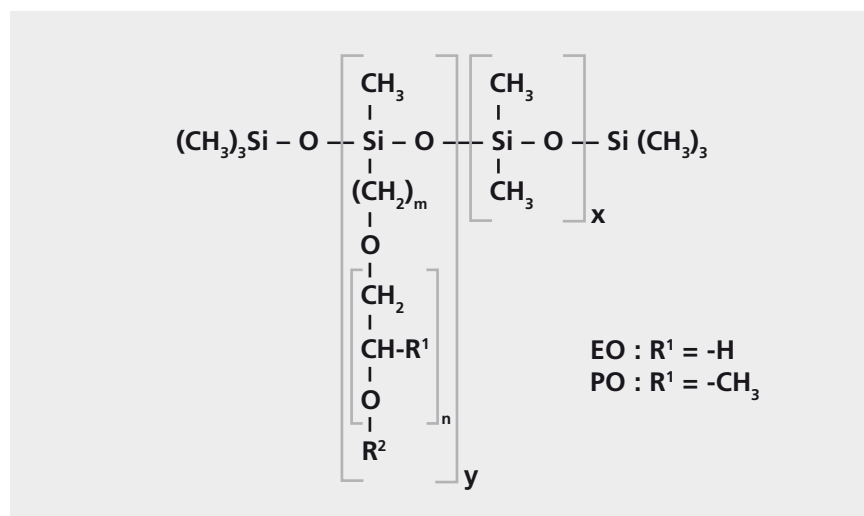


figure 6

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

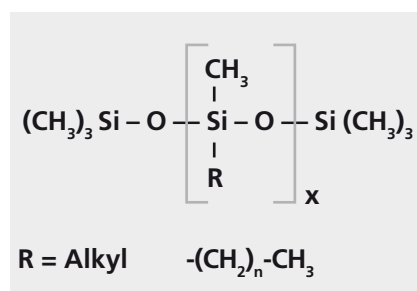


figure 7

Thermostable modified Polysiloxane

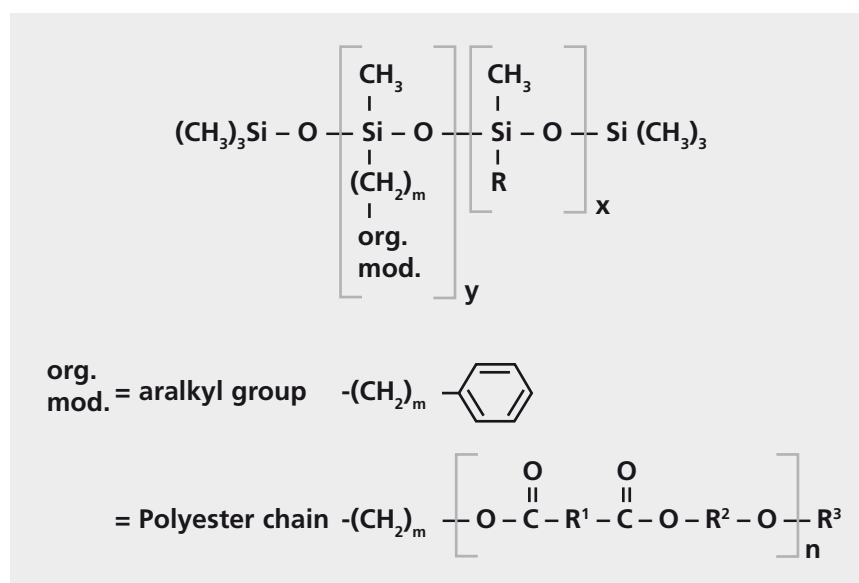


figure 8

› 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 (e.g. BYK-307).

Reactive Silicones

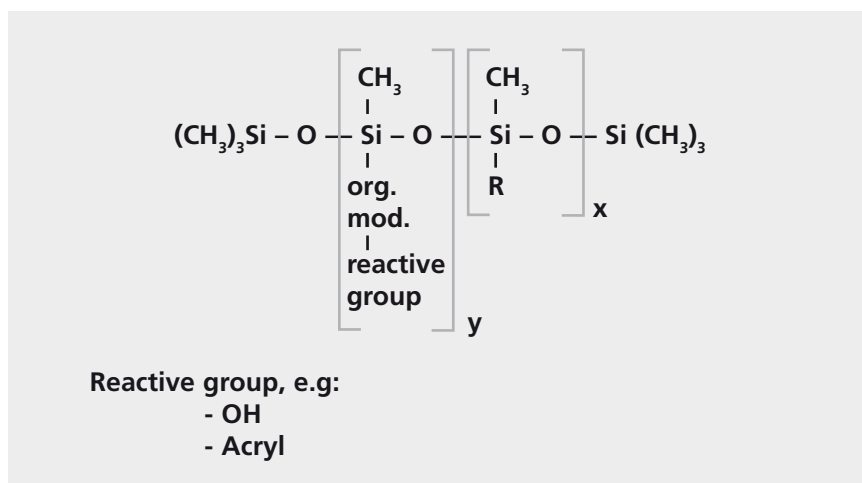


figure 9

Silicone Surfactant

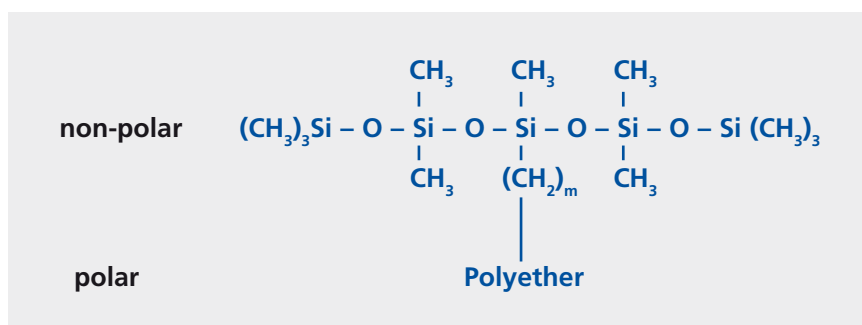


figure 10

Chemical Building Blocks of Polyacrylates

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

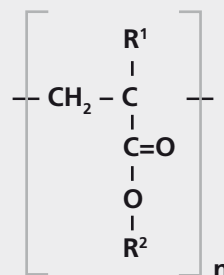
The C=C double bond site of this molecule can be polymerized to give long-chain polyacrylic acids. If methacrylic acid is used as a monomer instead of acrylic acid, then the corresponding polymethacrylates are formed.

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



R¹ = -H: Acrylate
-CH₃: Methacrylate

R² = Alkyl, polyether, polyester, salt

figure 11

Silicone Additives to improve Substrate Wetting

	Usage in solvent-borne system	Usage in aqueous system
BYK-306		
BYK-307		
BYK-310		
BYK-333		
BYK-344		
BYK-345		
BYK-346		
BYK-347		
BYK-348		
BYK-349		
BYK-378		
BYK-DYNWET 800		

figure 12

Substrate Wetting – I



Poor substrate wetting
on oily substrate



Perfect wetting
with BYK-306

figure 13

Substrate Wetting – II



Poor substrate wetting
of an aqueous coating on PVC foil



Perfect wetting
with BYK-346

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.

Silicone additives reduce the surface tension and accordingly, will lead to improved substrate wetting.

Of special interest here are silicones with dimethyl structures since this structure is capable of reducing surface tension (for example, BYK-378, BYK-306, BYK-310, BYK-333, BYK-341, BYK-344, BYK-307).

As mentioned previously, silicone surfactants BYK-346, BYK-345, BYK-347, BYK-348 and BYK-349 are particularly suited for waterbased systems.

BYK-DYNWET 800, a silicone free surfactant (based on alcohol alkoxylates) that provides low dynamic surface tension is also recommended for aqueous formulations.

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

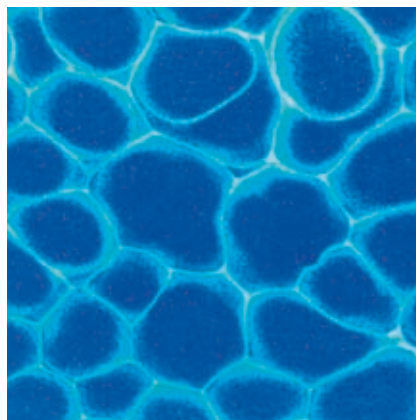


figure 15

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

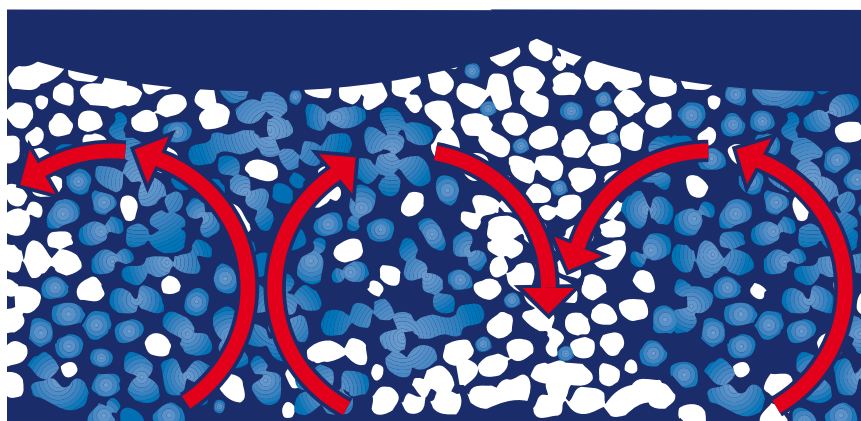


figure 16

Surface Flow Control – Leveling







During application		After application	
Surface flow control			
			
Typical example: Low solids spray-applied finish		Without surface flow control additive	With surface flow control additive (silicone)
Leveling			
			
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 (see also Technical Information L-WI 1). 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 (BYK-306); while high surface tension leads to comparatively long wave structures (BYK-320, BYK-331). For radiation curing systems, BYK-UV 3500, BYK-UV 3510 and BYK-UV 3530 are recommended.

To avoid aircraft sensitivity, BYK-330 is the most effective product from the entire range of silicone additives. Polyacrylates are considerably more important than polysiloxanes for improving leveling (see next chapter).

Problems solved with Acrylate Additives

Polyacrylate additives are mainly used for improving leveling. BYK-359, BYK-356/ BYK-355 and BYK-361N/BYK-358N are polyacrylates with a range of polarities designed to achieve optimal leveling in different paint systems.

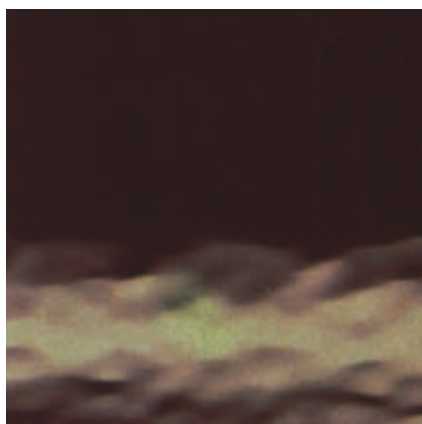
BYK-354 is much more incompatible because of its high molecular weight. Additionally it also provides good air release. BYK-380N and BYK-381 are suitable for waterborne systems due to their high polarity; BYK-380N can also be used in solvent-borne formulations. BYK-390 is not a typical flow additive, it is used in solventbased baking systems for antipopping and is often combined with other acrylates. BYK-392 combines anti-popping with improved leveling. Along with surface tension considerations, the rheology of the coating can also have significant impact on surface flow. In addition to the influence on surface flow by rheology modifiers, wetting and dispersing additives can also contribute considerable influence. In many cases, surface flow problems cannot be solved by surface flow control additives alone; the other constituents of the formulation must be taken into consideration.

For **powder coating** applications acrylate leveling additives are available in powder form. In these cases the polyacrylates are absorbed onto a porous silica carrier.

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 cases where the most effective surface tension lowering agents are required, polydimethylsiloxanes such as BYK-378, BYK-306, BYK-307, BYK-333 or BYK-310 should be used for anti-cratering. Polyacrylates have only slight influence on surface tension, and therefore do not work as anti-cratering additives.

Craters

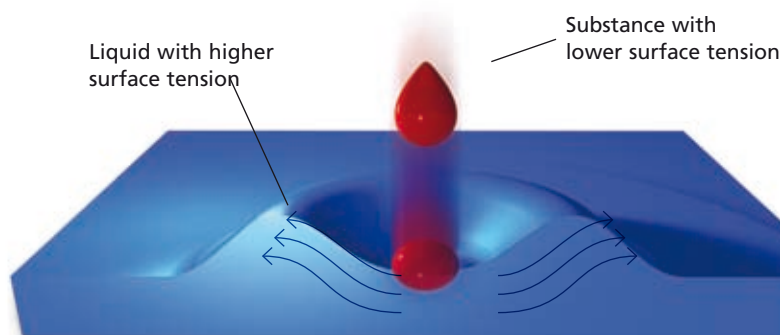


figure 19

Defoaming

Foam can be caused by the improper use of silicone additives. However, the proper use of silicone additives will result in the removal of foam. Of fundamental importance in distinguishing between proper and improper performances, are both the polarity and the compatibility of the silicone additive. Highly compatible silicone additives with low surface tensions tend to stabilize foam. In special cases where highly compatible products cause foam problems, products with higher surface tensions (for example, methylalkyl modified products: BYK-320 or BYK-322) should be used. These products are not defoamers but are rather silicone flow additives with defoaming properties. In cases where true defoamers are needed, more incompatible products such as BYK-077 (an unmodified methylalkylpolysiloxane) should be considered. With sufficient incompatibility, polyacrylates (such as BYK-354) also exhibit defoaming properties. Detailed information about defoamers (silicone-containing or silicone-free) can be found in the Technical Information brochure L-DI 1 – Defoamers. ➤

› Uses for Surface Additives

Increase of Surface Slip

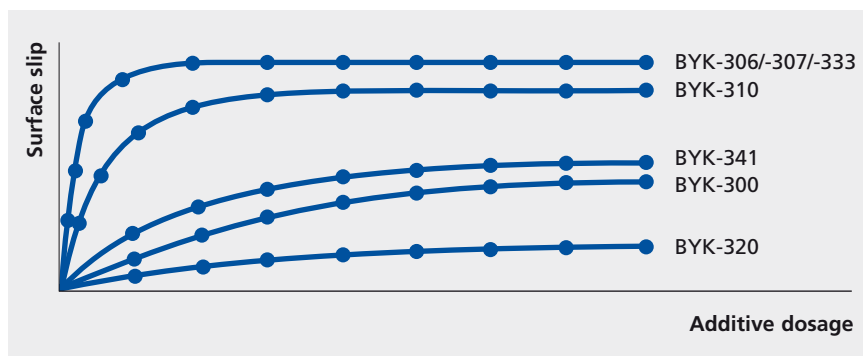


figure 20

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. If slip improvement is the primary goal, the choices are BYK-378, BYK-306, BYK-307, BYK-333, BYK-341 and BYK-310.

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

In furniture coatings, as well as other applications, tape release is desirable: adhesive tapes as well as all kind of stickers should be easily removed from the surface without leaving residual adhesive or damaging the surface. Silicone additives are suitable for improving tape release. For solvent-borne, solvent-free and aqueous systems BYK-UV 3500 is recommended. Its acrylic functionality allows incorporation into the binder matrix in radiation curing systems. In non-aqueous formulations, BYK-UV 3510 can be used.

The silicone-free BYK-394 improves the release of protective foils from coil coatings or other solvent-borne coatings.

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.

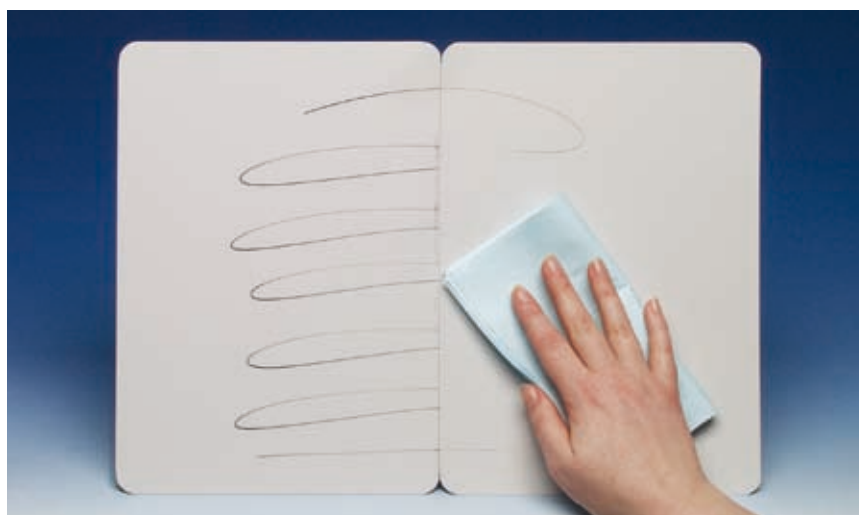
Easy Surface Cleaning



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

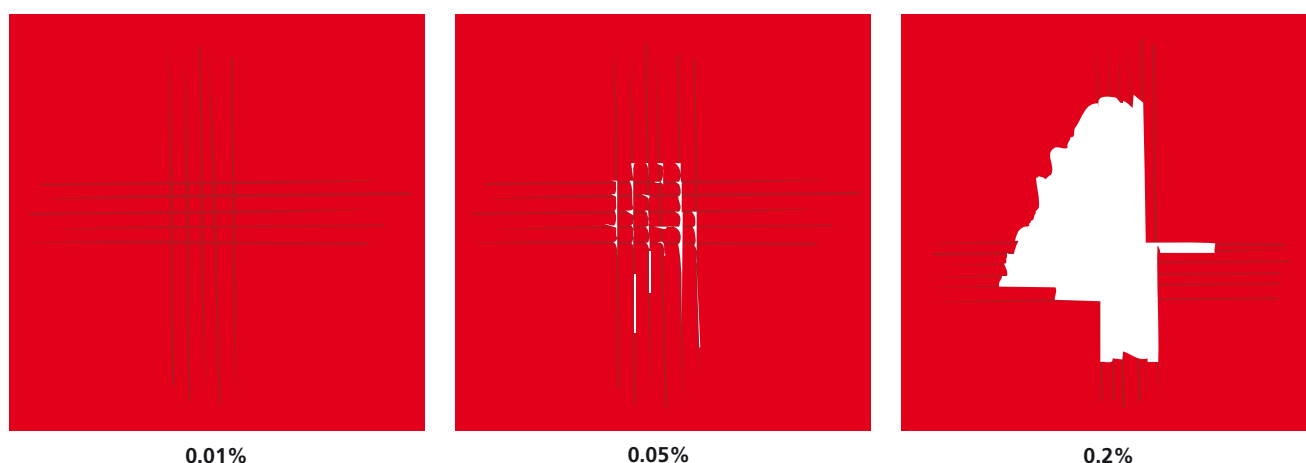
Silicone Additives and their Influence on Intercoat Adhesion

Silicones as a general class of products have an unearned reputation in the industry for being un recoatable 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.

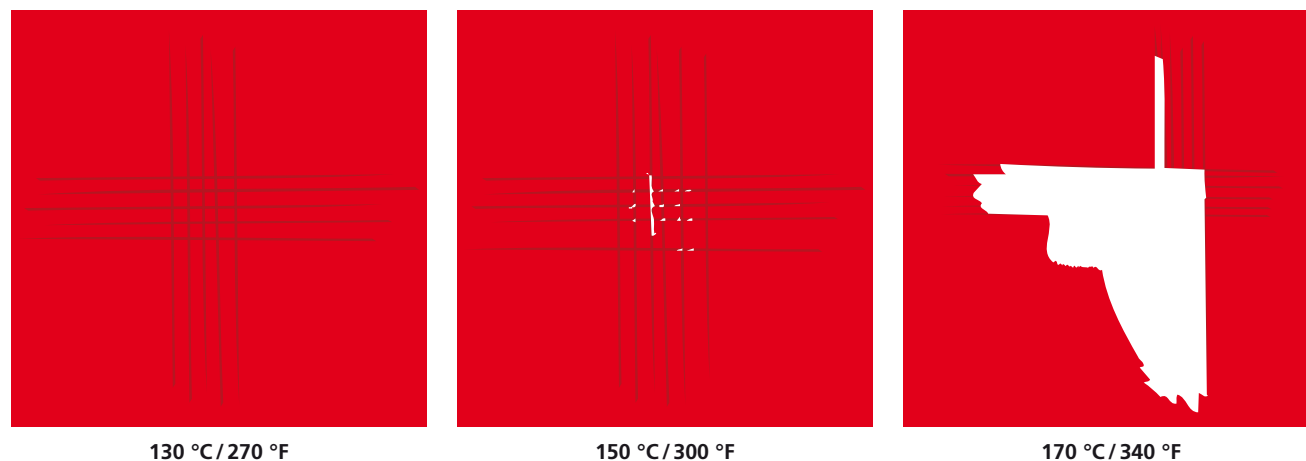
Influence of Silicone Dosage



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 overdose 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.

Corresponding BYK products are BYK-310 and BYK-322.

Products and Applications

BYK Additives

Additives are used during the production of coatings, printing inks and plastics to optimize the production process and to improve the quality of the final product.

Product Range Additives

- Additives to improve surface slip, leveling and substrate wetting
- Adhesion Promoters
- Defoamers and air release agents
- Foam stabilizers
- Processing additives
- Rheological additives
- UV-absorbers
- Viscosity depressants
- Waxes
- Wetting and dispersing additives for pigments and extenders

Application Areas

- Ambient curing resins (FRP)
- Architectural coatings
- Automotive OEM
- Automotive refinishes
- Can coatings
- Coil coatings
- Color masterbatches
- Industrial coatings
- Leather coatings
- Marine paints
- Molding compounds
- Paper coatings
- Pigment concentrates
- Polyurethane foams
- Powder coatings
- Printing inks
- Protective coatings
- PVC plastisols
- Thermoplastics
- Wood and furniture coatings

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