

PAINTS AND COATINGS - HOW SURFACTANTS CAN ADVANCE NEW DEVELOPMENTS

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Coatings are multi-component systems and surfaces/interfaces have a strong influence on their quality and play also an important role during paint application. Coating additives are used since many years successfully as "problem solvers" in coating formulations to overcome defects and in general to improve the overall quality. Many coating defects are closely connected with interfacial phenomena and therefore it is no surprise that oftentimes coating additives are surface active materials.

Examples of typical coating defects are shown together with problem solutions using surface active coating additives. The development of coating additives is mainly driven by market needs. In the past excellent quality and performance had a very high priority. During the last 15 to 20 years the focus shifted more and more to ecological considerations. Less pollution of water and air is required and the range of raw materials from which the paint chemist can choose has shrunken (e.g., no more lead pigments, no more aromatic solvents). These changes are a constant challenge for additive producers. Coating additives normally do not trigger new developments in coatings but they can be the crucial factor to make a new and innovative coating system successful in the market.

1. Interfaces in Coatings

In paints and coatings many interfaces exist and their properties can be modified with surface active materials. Such surfactants oftentimes are used in fairly small quantities (below 1%) and are termed "additives" in coating technology. A typical example in a liquid coating is the interface between the liquid resin solution and solid particles such as pigments and extenders. Wetting of the pigment particles and stabilization of the pigment dispersion (to avoid flocculation) are important properties which can be controlled via this interface. In several situations gas bubbles (mainly air) are created in the liquid coating. The interface air/liquid is responsible for the stabilisation of these bubbles ("foam") and also for their destruction by defoaming additives.

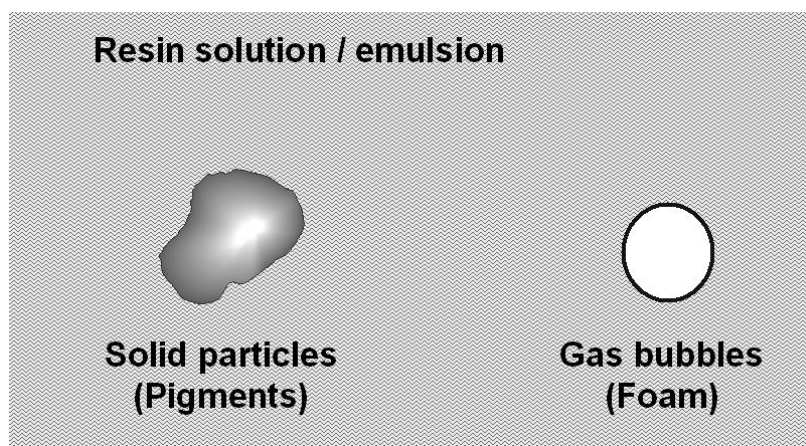


Figure 1: Interfaces in a liquid coating material

After application of a coating on a substrate other interfaces become important as well. The interface between the coating film and the substrate controls, among other properties, substrate wetting and adhesion. The surface of the coating film (interface coating/air) is responsible for flow and leveling of the coating, mechanical properties such as surface slip (friction) and others.

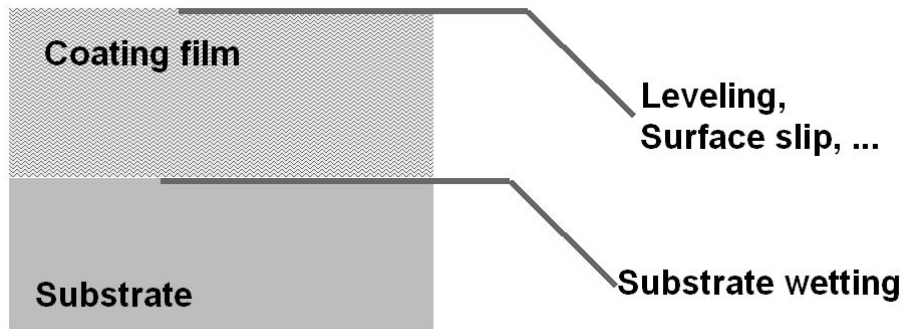


Figure 2: Interfaces in coating film and relevant properties

In the following discussion we will focus on two typical examples how surface active additives can successfully overcome coating defects. The first example deals with pigment stabilization and the usage of wetting and dispersing additives and the second example is about special silicone additives to improve substrate wetting. In both cases it will be shown that the development of new types of surface active additives was necessary to fulfil the changing requirements of the coatings industry.

2. Wetting and Dispersing Additives

One of the most important steps in the production of pigmented coatings is the homogeneous distribution of *solid* pigments within the *liquid* binder solution (or binder emulsion). If this pigment grinding step is not optimized, then a wide variety of defects can occur:

- Flocculation
- Gloss decrease
- Color shift
- Flooding/floating
- Settling
- Viscosity instabilities

The Dispersing Process

Pigment agglomerates are reduced in size during the pigment grinding phase; ideally this leads to the production of primary particles. Agglomerates represent pigment clusters in which the interstitial spaces between the individual pigment particles contain air and moisture. These individual pigment particles are in contact with one another only along their edges and corners. Interactive forces between the particles are relatively small so that such forces can be overcome by traditional dispersing equipment. In the dispersing phase, energy is added to the system and therefore smaller particles (with a larger interface to the resin solution) are formed. The system then endeavors to escape this energy-rich state in order to revert to its previous low energy condition. This is evidenced by the finely distributed pigments coming back together to form flocculates. Effects such as reduced color strength, decreased gloss, and altered rheology then occur.

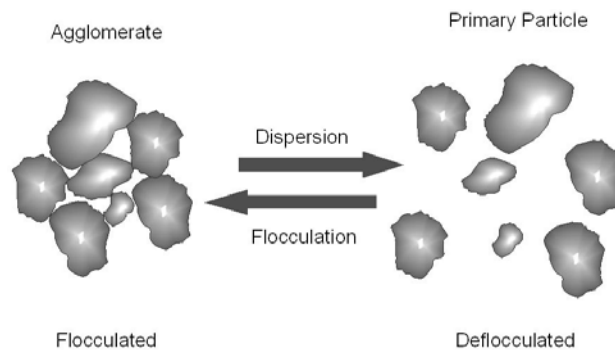


Figure 3: Pigment dispersion and flocculation

The various processes which occur during pigment grinding can be divided into the following three steps:

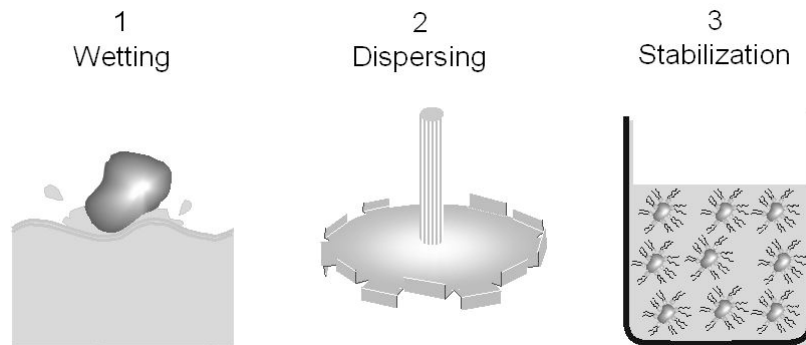


Figure 4: Details of the wetting and dispersing process of pigments

During **Step 1 (Wetting)**, all of the air and moisture at the pigment surface is driven off and then replaced by the resin solution. The solid/gaseous interface (pigment/air) is transformed into a solid/liquid interface (pigment/resin solution). The resin solution must penetrate into the space between the agglomerates.

Step 2 (Grinding) represents the true pigment grinding stage. Through mechanical energy (impact and shear forces), the pigment agglomerates are broken up and accordingly reduced in size.

In the concluding **step 3 (Stabilisation)**, the pigment dispersion must be stabilized in order to prevent the formation of uncontrolled flocculates. As described later, special techniques make it possible to keep the pigment particles at appropriate distances from one another so that they do not resume contact. In most applications the stabilization of the deflocculated condition is desirable.

Steps 1 (wetting) and 3 (stabilizing) can be influenced by additives. *Wetting* additives accelerate the wetting of pigment agglomerates by the resin; *dispersing* additives improve the stabilization of the pigment dispersion. One and the same product can oftentimes function as both the wetting and the dispersing additive.

Wetting Additives

The wetting of pigment agglomerates through the resin solution is influenced by many factors. The penetration speed of the liquid phase into the space between the agglomerates is - under considerably simplified conditions - mathematically expressed by the Washburn equation. Influential factors include the polarities of the pigment surface and of the binder solution; the viscosity of the liquid phase; and also the geometry of the empty spaces (or pores) within the agglomerate structures. Of special importance is the interfacial tension in the exact areas where the wetting additive performs - between the pigment surfaces and the resin solution.

Wetting additives can be defined as substances which are designed to reduce interfacial tension and which, as a result, increase the "spreading pressure" so that the wetting process is accelerated. Characteristic for such substances is their surface-active structure: polar, hydrophilic structural elements along with nonpolar, hydrophobic structural elements combined in one molecule. Because of this very structure, such molecular combinations are interfacially active.

From a chemical standpoint, wetting additives can be classified as either ionic or non-ionic - according to the chemistry of the polar segment in the molecule. The nonpolar segment is, as a rule, represented by hydrocarbon chains.

Dispersing Additives

Dispersing additives adsorb onto the pigment surface and therefore maintain proper pigment spacing through steric stabilization, thus reducing the tendency towards uncontrolled flocculation. Also electrostatic charges can be employed, however, this mechanism will not be discussed in this paper.

Dispersing additives which function by steric hindrance display two special structural features. First, such products contain one or more so-called “pigment-affinic” groups - anchor groups or adhesive groups – that all together provide a strong, durable adsorption onto the pigment surface. Second, such products contain resin-compatible chains (hydrocarbon entities) which, after adsorption of the additive onto the pigment surface, protrude as far as possible from the pigment into the surrounding resin solution. This layer of adsorbed additive molecules with the protruding chains is referred to steric hindrance or entropic stabilization.

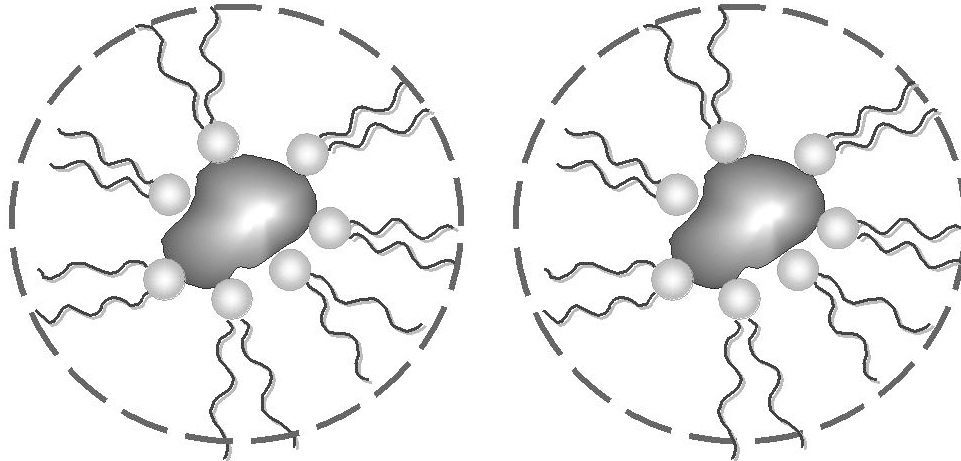


Figure 5: Steric stabilization of pigment particles to avoid flocculation

The above stabilization is further accentuated by the interaction of the additive’s polymeric segments with the resin polymers in such a way that the “envelope”, so to speak, around the pigment particles is enlarged. Through specific structural elements composed of pigment-affinic groups (polar) and resin-compatible chains (nonpolar), these additives exhibit definitive surface-active properties. In other words, they not only stabilize the pigment dispersion, but they also function as wetting additives.

Low-molecular weight and polymeric wetting and dispersing additives

The structure of the classical deflocculating additives has already been described as one or more spatially close pigment affinic groups and a number of resin-like chain structures. These classical wetting and dispersing additives are based on fatty acid chemistry and are used in coatings since many years. They are ideal to stabilize inorganic pigments and extenders because such particles exhibit a fairly polar surface area and the adsorption of the additives is strong enough to guarantee excellent pigment stabilization. A durable and permanent adsorption onto the pigment surface is of utmost importance for the stabilizing efficiency of wetting and dispersing additives.

With organic pigments however, the situation is different. These pigment crystals are composed of individual molecules which themselves are dominantly nonpolar. As a result, organic pigments have very nonpolar surfaces and therefore make proper adsorption of conventional additives rather difficult. In practice, this means that organic pigments are insufficiently deflocculated and stabilized by traditional wetting and dispersing additives.

Organic pigments became more and more popular, mainly because they had to replace inorganic lead-containing pigments which were banned in most countries. It became then obvious, that the conventional (low molecular weight) wetting and dispersing additives could not achieve the required stabilization of these organic pigments, especially in areas where the quality level was very high, such as automotive coatings.

For the above reason, a new group of additives has been developed over the past few years - high molecular weight polymeric wetting and dispersing additives. Such additives differentiate themselves from the conventional low molecular weight polymers through considerably higher molecular weights which allow the attainment of a resin-like character. In addition, the newer additives contain a considerably higher number of adhesion groups. Because of these structural features, such additives can form durable adsorption layers upon many organic pigments. Stabilization arises from steric hindrance (as with the conventional products) in which well solvated polymer chains are utilized.

Optimal stabilization is possible only when such polymer chains are properly unfurled and therefore quite compatible with the surrounding resin solution. If this compatibility is obstructed, then the polymer chains collapse. Consequently, all chances for steric hindrance and the resultant stabilization are lost. The compatibility of a high molecular weight polymeric product with various coatings resins is considerably more restricted than that of a low molecular weight variety. Accordingly, an entire family of chemically related additives (classified according to molecular weight, polarity and compatibility) is available. Even though the polymeric wetting and dispersing additive were developed for organic pigments, they may also be utilized equally as well with inorganic pigments.

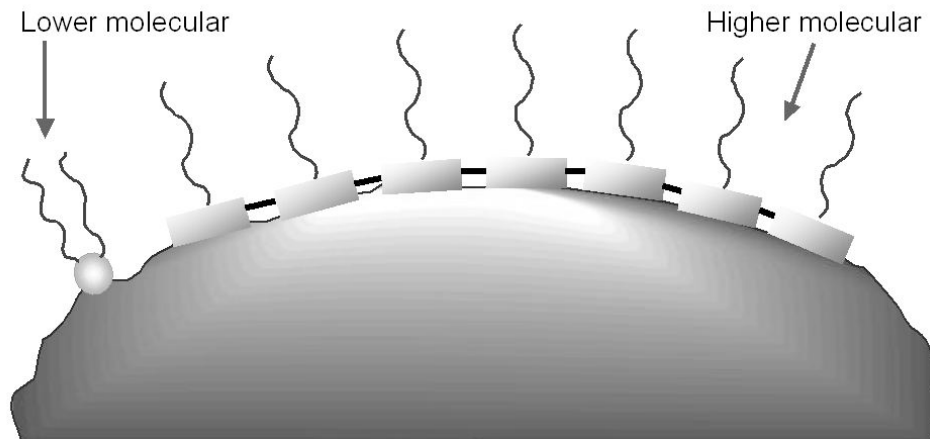


Figure 6: Comparison of low molecular weight and high molecular weight (polymeric) wetting and dispersing additives

Prevention of flooding and floating

Most pigmented coating systems contain more than one pigment type. Flooding and floating occur when the various pigments separate from one another and are no longer homogeneously distributed. If, in the paint surface, local differences in concentrations occur, one speaks of "horizontal" floating. This results in Bénard cells, silking or streaking. The paint surface then does not show a homogeneous color, but a dotted, silky one. If there are no concentration differences in the paint surface, but there are in the vertical direction, the phenomenon is called "vertical" flooding. In this case the coating layer shows a uniform color; the defect is only visible when the "rub-up" test (see below) is utilized. This latter defect is quite common in many paint formulations with more than one pigment, whereas the "horizontal" floating shows up fairly seldom.

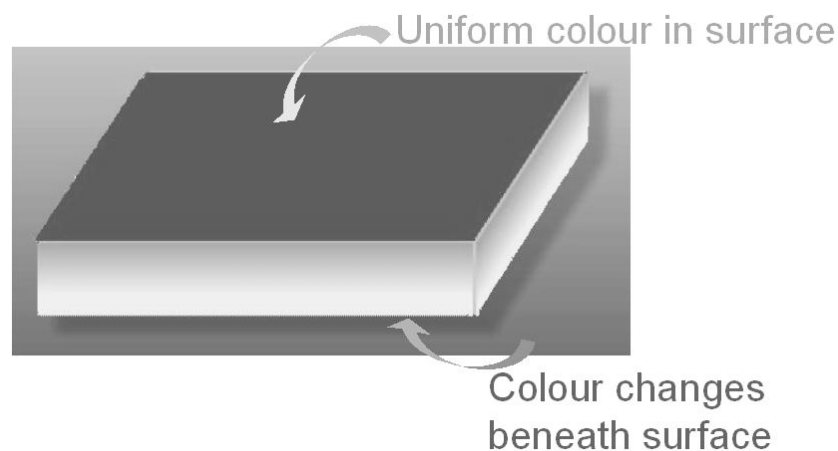


Figure 7: Instable pigment mixture where one pigment concentrates in the surface ("vertical" flooding)

Differences in pigment mobility is often the decisive factor that causes pigments to no longer be homogeneously distributed. When solvents evaporate from a paint film, eddies and currents form within the film. Such movements inside the film can be traced back to small intra-film differences in temperature, density, and surface tension. The pigments naturally participate in such movements; and when differential pigment mobilities occur - pigment separation along with flooding and floating occur.

Differential mobility can be equilibrated through the usage of appropriate wetting and dispersing additives. Through the intense interaction of the adsorbed polymeric additives with the surrounding resin solution, the deflocculated pigment particles are tightly incorporated into the resin system. Consequently, the mobility is then no longer determined by particle size and density; in contrast, the overwhelming factor is this interaction. This explains how flooding and floating can be eliminated even in the presence of smaller, deflocculated organic pigment particles and larger, inorganic pigments. The polymeric wetting and dispersing additives are especially helpful, because they can stabilize both inorganic and organic pigments extremely well.

“Rub-up” test

To demonstrate that a given pigment mixture in a coating is not perfectly stabilized against pigment separation the so-called “rub-up” test is used. The coating is applied to a solid substrate and then, while the paint film is still wet, part of the film is rubbed with a finger. In this area the pigment mixture is completely homogenized by the rubbing movement. A color difference between the rubbed area and the area which was not touched indicates an instable pigment mixture. If all pigments in the mixture are perfectly stabilized, no color difference should be visible.

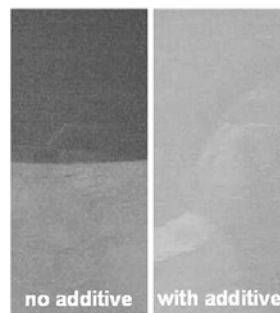


Figure 8: Rub-up test of a coating containing two pigments (bottom part of paint film is rubbed). Left side: color difference indicates instable mixture. Right side: no color difference due to perfect stabilization with additives.

3. Substrate Wetting with Silicone Surfactants

When a liquid coating is applied on a substrate, it is expected, that it will wet that substrate easily and evenly. Good wetting is necessary for an optically perfect surface, good adhesion to the substrate and full functionality of the coating (substrate protection).

Most important for the substrate wetting are the surface tension values of the involved materials: the liquid coating and the solid substrate. In general, for good substrate wetting the surface tension of the coating material (σ_p) should be lower than the surface tension of the substrate (σ_s); at least they should be equal.

$$\sigma_p \leq \sigma_s$$

If the surface tension of the coating material is higher than that of the substrate poor wetting may occur. The real reason for improper substrate wetting is the too high surface tension of the liquid coating, however, other factors will also have an influence how strongly this defect will show up. Film thickness, e.g., is quite important: wetting problems are easily seen in thin coating layers, high film build can eventually cover the defects. In a similar way also the viscosity/rheology of the coating plays an important role: low viscous systems with a more newtonian flow behaviour will show substrate wetting problems at once, whereas high viscous systems will not show the defects at all.

Influencing the surface tension of coatings

The surface tension of the liquid coating is primarily defined by the selection of the resins and the solvents; the pigments have no influence. In practise, however, selection of these raw materials is normally not based on their surface tension but on other properties. Resins are selected regarding, e.g., their crosslinking mechanism, the required chemical resistance and the mechanical properties of the dry film. For the solvents it is important that they can easily dissolve the resins in questions; other properties which have to be observed are their evaporation behaviour, their flash point and - getting more and more attention in these days - their ecological performance.

Therefore it is very convenient to control the surface tension of the liquid paint independently from other raw materials by suitable additives. It was shown above that improvement of substrate wetting requires a reduction of the surface tension of the coating. Additives which can do exactly this are polysiloxanes and fluoro surfactants. Polysiloxanes modified in many ways ("silicone additives") have found broader usage than the fluoro compounds. Silicone additives are very versatile products and they are used in coatings for more reasons than just surface tension reduction (e.g., surface slip, leveling, defoaming).

Chemistry of silicone additives

The term "silicones" is used for a wide variety of different chemical products which are used in many different technical application areas. Only a small segment of this chemistry is suitable as additives for paints and coatings.

All silicone additives for coatings are based on the relatively simple chemical structure of the polydimethylsiloxanes. The backbone consists of several Si-O- units (siloxane units), where each silicon atom carries two methyl groups. One way to modify this structure is to vary the chain length and thus the molecular weight. Higher molecular weight means reduced solubility in coating systems and lower compatibility. Products with a very high molecular weight are so incompatible and insoluble in most coating systems, that they create craters in a very defined and reproducible way and therefore can only be used for special effect coatings like hammertone finishes.

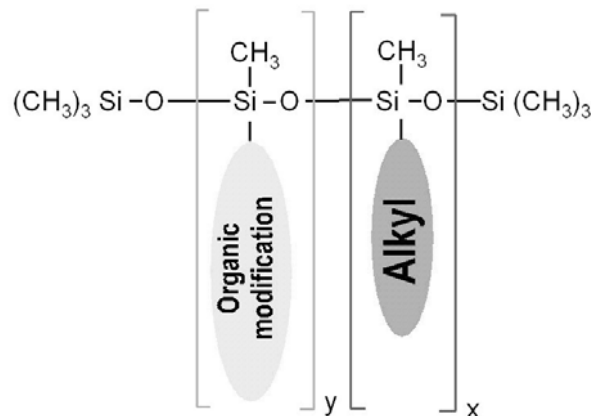


Figure 9: Chemical structure of organically modified polysiloxanes

To modify the properties of the polysiloxanes it is possible, besides varying the chain length, to replace the methyl groups (partly) by other side chains, the resulting products than are termed "organically modified" polysiloxanes. This organic modification is a very elegant method to control the compatibility of these structures with coating systems. These organic side chains improve the compatibility and the above mentioned influence of the molecular weight of the polysiloxane backbone becomes less important. In most cases the polysiloxanes are modified with polyether chains. This way of modification offers so many possibilities, that silicone additives with very specific property profiles can be synthesized, tailor-made for the various requirements of many application areas.

The dimethyl groups are responsible for a low surface tension of the silicone additives and variation of the ratio dimethyl groups to polyether modifications (x:y) therefore offers an ideal way to adjust the surface tension to specific values. There still is the additional possibility to influence the surface tension by replacing some of the remaining dimethyl structures by methylalkyl groups. This further increases the surface tension of the silicone and the surface tension reduction effect of the additive is reduced accordingly.

Furthermore the structure of the polyether chain itself can be modified. These polyethers basically are build from ethylene oxide units (EO) and propylene oxide units (PO). Polyethylene oxide is quite hydrophilic (polar), whereas polypropylene oxide is hydrophobic (non-polar). The EO/PO ratio therefore controls the overall polarity of the silicone additive: high EO amounts increase the polarity and the additive becomes more compatible in polar coating systems and the additive even may become water-soluble. However, at the same time also its tendency of foam stabilization increases. High PO amounts on the other hand reduce water-solubility and increase defoaming properties.

Silicone surfactants

As shown above, by adjusting the polarity it is possible to synthesize silicone additives which are compatible with aqueous coating systems. However, oftentimes it is observed, that the efficiency of such additives is not sufficient, especially when wetting of low energetic substrates (plastics) is concerned. The water content in these coating systems creates a relatively high surface tension (higher than in solvent-based coatings) which is reduced by the silicone additives, but oftentimes is still too high for good wetting. For such cases a special class of silicone additives was created: silicone surfactants. Chemically these additives also are polyether modified siloxanes, but their molecular weight is much lower, resulting in a pronounced surfactant-like structure. Due to this structure these additives strongly reduce the surface tension in aqueous systems; they are nearly as active as fluoro surfactants. Compared to the fluoro surfactants the silicone surfactants, however, have one important advantage: foam stabilization by silicone surfactants is nearly absent, whereas fluoro surfactants are not always unproblematic in this respect.

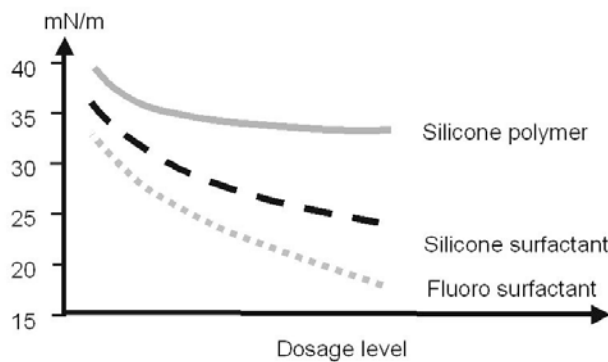


Figure 10: Reduction of surface tension in water by different additives

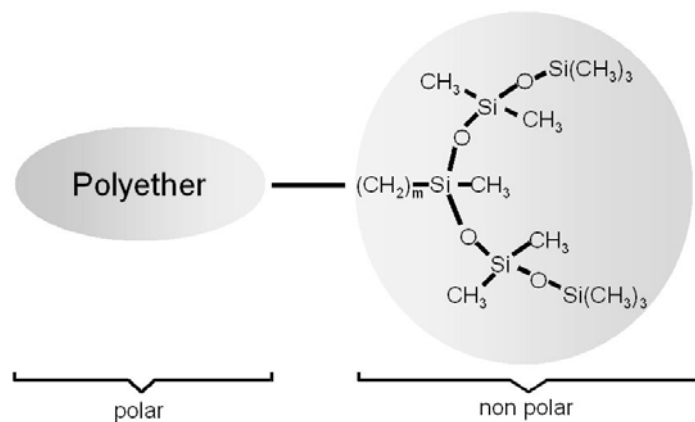


Figure 11: Chemical structure of silicone surfactants

A practical example is shown in Figure 12. A PVC foil had to be coated with an aqueous clearcoat. Without a suitable additive the clearcoat shows very poor wetting, it crawls back from the substrate and no closed paint film can be formed. Usage of a silicone surfactant reduces the surface tension of the clearcoat to such a level that now substrate wetting is perfect. Substrate wetting is a general problem in many aqueous coatings systems and silicone surfactants are the ideal tool to overcome these problems.

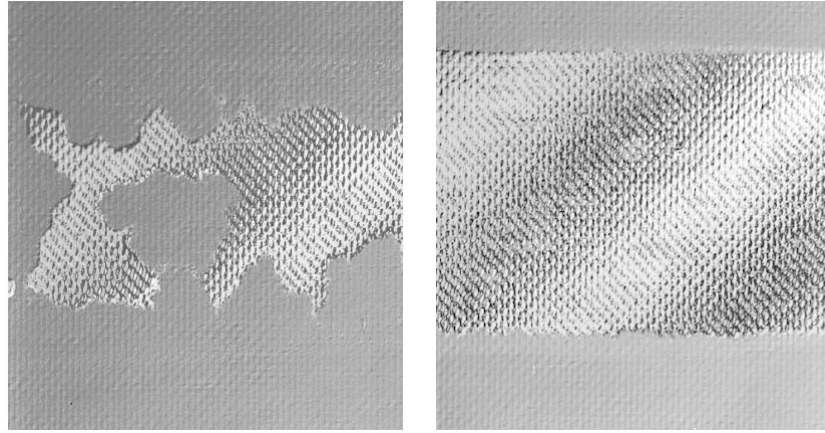


Figure 12: Wetting of an aqueous clearcoat on a PVC substrate. Left side: poor wetting. Right side: excellent wetting due to a silicone surfactant.

4. Summary

Coatings additives normally do not trigger new developments in coatings but they can be the crucial factor to make a new and innovative coatings system successful in the market. Two examples were used to demonstrate this.

Modern coatings make no longer use of lead pigments but organic pigments are used instead. To stabilize organic pigment particles polymeric wetting and dispersing additives had to be developed as a new generation of wetting and dispersing additives. Today such materials are widely used in the coatings industry and guarantee a very high quality level.

Likewise, the trend from solvent-based formulations to aqueous coating systems created oftentimes problems, especially the substrate wetting of water-based paints is far from ideal. Conventional silicone additives are not efficient enough in many aqueous coatings and only the new silicone surfactants can overcome this severe drawback and help these innovative systems to get their market share.

5. Bibliography

Johan Bieleman (ed.): Additives for Coatings, Weinheim 2001

Only one reference is given, because this textbook covers the whole range of additives for coatings and most of the relevant literature is cited here.