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little helpers love great achievements

Practical Guide to Wetting Agents and Surface Modifiers

Formulation Additives by BASF

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BASF

the world’s leading chemical company, is a premier provider of innovative solutions for the paints and coatings industry. BASF offers virtually every ingredient needed to make high quality coatings – along with the know-how to solve formulation challenges and support the development of new coating concepts. Our portfolio encompasses dispersions, pigments, resins and a broad range of additives such as light stabilizers and formulation additives.

When it comes to formulation additives, BASF offers a strong portfolio of industry-leading products that help to enable sustainable and performance-driven solutions. Our offer comprises the broadest technology base of dispersing agents, wetting agents & surface modifiers, defoamers, rheology modifiers and film forming agents.

We put our understanding, listening & collaboration skills at the forefront to serve our customer’s needs. With global manufacturing capabilities, a strong research and development platform, full-service regional technical laboratories, pre-screening capabilities and a team of knowledgeable, experienced experts, BASF can help to make your coatings better and your business more successful.

This booklet has been developed in order to give paint formulators and technicians initial guidance on the use of Wetting Agents and Surface Modifiers from BASF and on making the most out of their performance characteristics.

Looking for innovative solutions where little helpers make all the difference for your high quality coatings?

BASF - We create chemistry

Table of Contents

Wetting Agents and Surface Modifiers: An Introduction

Wetting agents and surface modifiers are essential components of modern paints and coatings. They provide a formulation with adequate wetting properties, enhance different component compatibility and improve the surface of a coating. Our broad portfolio of wetting agents and surface modifiers offers highly effective products for almost every paint, coating and ink system.

Most coating systems need good flow and leveling in order to have a smooth appearance. A flat and even surface will give a higher gloss and is therefore eye catching. As shown in Figure 1, wetting agents and surface modifiers can have a strong influence on coating properties like substrate wetting, slip, flow and leveling.

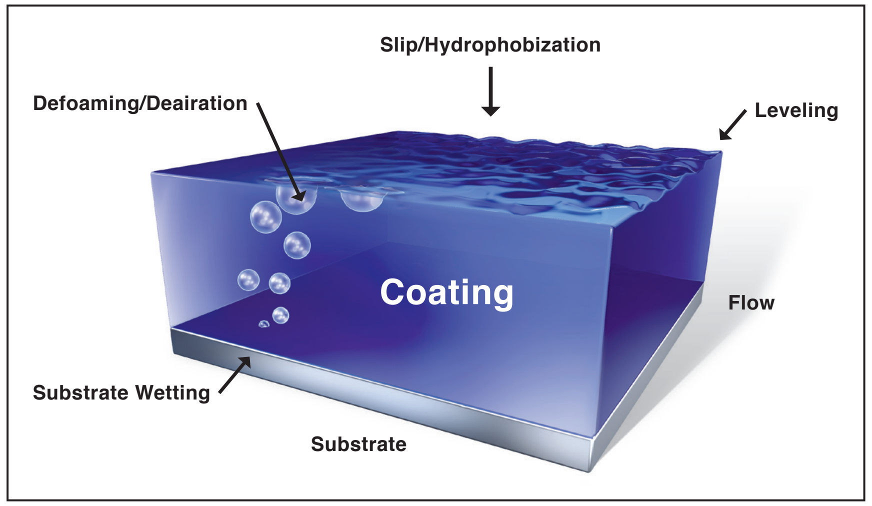
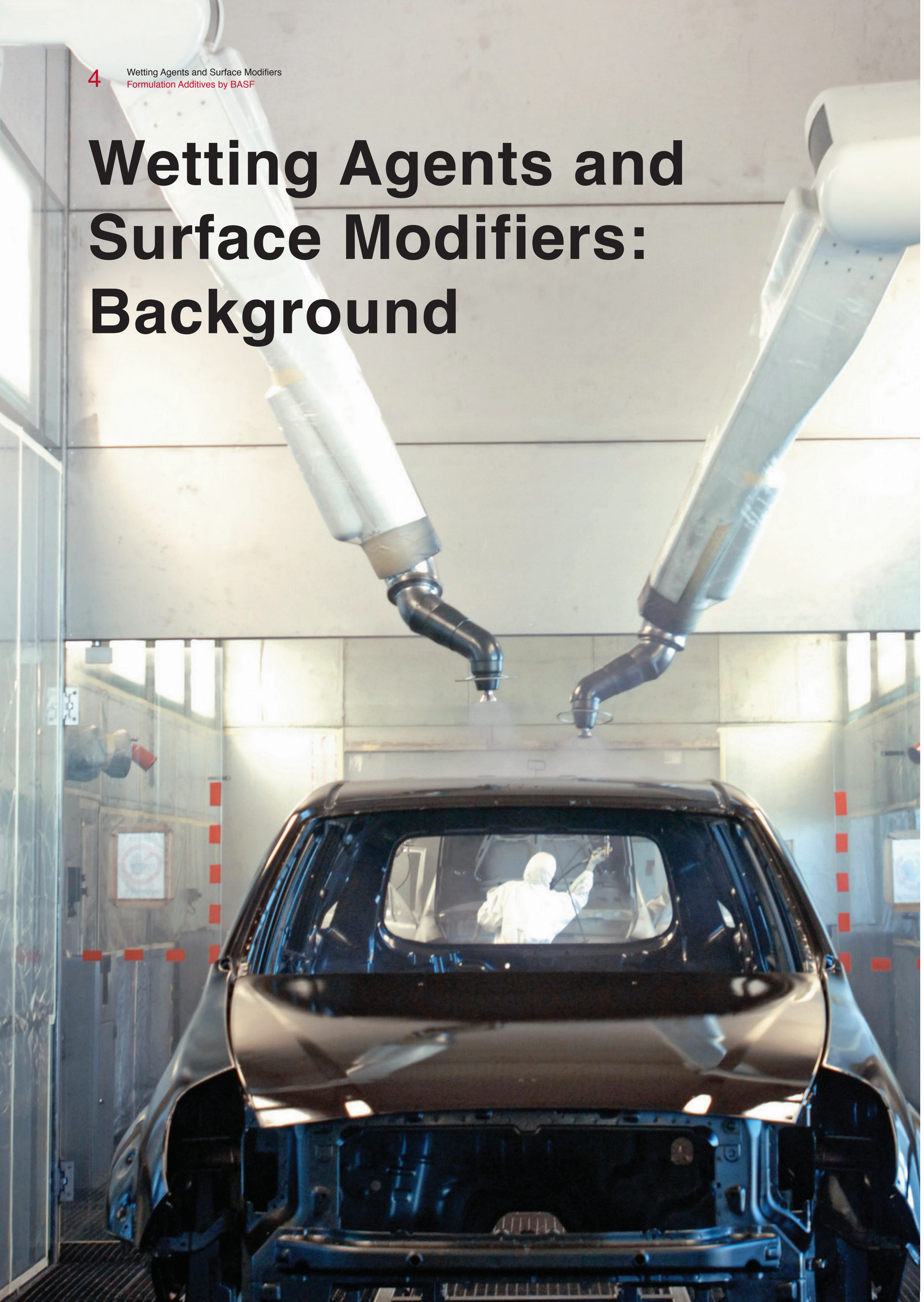


Figure 1:
Several coating effects like substrate wetting, flow & leveling, surface slip and defoaming are controlled by wetting agents and surface modifiers

It is important to understand that coating effects like substrate wetting, foam formation, flow and leveling and slip are interdependent properties. For example, a substrate wetting agent may influence foam formation and a slip agent may impact the flow and leveling.

All wetting agents and surface modifiers are interfacially active substances. Their points of action are at interfaces like liquid/air (e.g. foam), liquid/solid (e.g. substrate wetting) or liquid/liquid (e.g. compatibility). A more detailed technical discussion of the fundamentals of interfacial effects, surface tension and related effects is given in the subsequent pages.

Wetting Agents and Surface Modifiers: Background



Wetting Agents and Surface Modifiers: Background

Surface Tension

In general, the term “surface” is used for the boundary between a condensed phase (liquid or solid) and a gas or a liquid. The term ‘interface’ is used to describe the junction between the two phases.

Surface tension can be best explained by the behaviour of molecules at the surface of a liquid. Cohesive forces between the molecules in the surface layer are not evenly distributed to all sides compared to molecules in the inner phase. The result of these unbalanced attraction forces is the so-called surface tension.

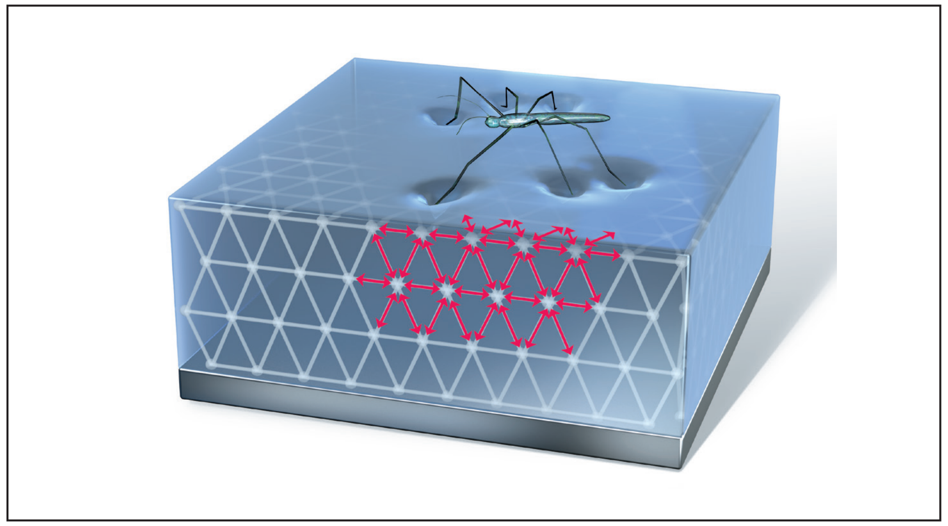


Figure 2:
Cohesive forces between the molecules in a surface layer are not evenly distributed, resulting in the surface tension

Surface tension is defined as the work (energy) that is needed to increase the surface by a defined area. For surfaces of solid materials the term "surface energy" is commonly used. The surface energy of solid surfaces can be indirectly determined by contact angle measurements with liquids with a known surface tension (see also Young equation). Consequently, the surface tension is typically given in units of mJ/m², dyn/cm or mN/m. In Table 1, typical surface tension values are given for various solvents and materials:

Solvents		Resins		Substrates	
Water	72 mN/m	Melamine resin	58 mN/m	Glass	70 mN/m
Ethylene glycol	48 mN/m	Epoxy resin	47 mN/m	PVC	40 mN/m
Xylene	32 mN/m	Polyester	41 mN/m	Polyethylene	33 mN/m
Butyl acetate	28 mN/m	Long-oil alkyd	26 mN/m	Polypropylene	28 mN/m

Table 1: Surface tension or surface energy values for various solvent and materials

Wetting Agents and Surface Modifiers: Background

There are several methods to measure the surface tension of a liquid. A common method to measure the so-called **"static surface tension"** is the Noüy Ring method. This method involves slowly lifting a ring, often made of platinum, from the surface of a liquid. The force required to raise the ring from the liquid's surface is measured and correlates with its surface tension. For fast application processes like printing or roller application it can be interesting to understand also the **"dynamic surface tension"** behaviour of a system. The dynamic surface tension can be measured with a bubble pressure tensiometer for example. A bubble pressure tensiometer produces gas bubbles at a specified rate and blows them through a capillary, which is submerged in the sample liquid. In this process, the pressure required to generate the new interface within the liquid passes through a maximum, which is directly related to the dynamic surface tension.

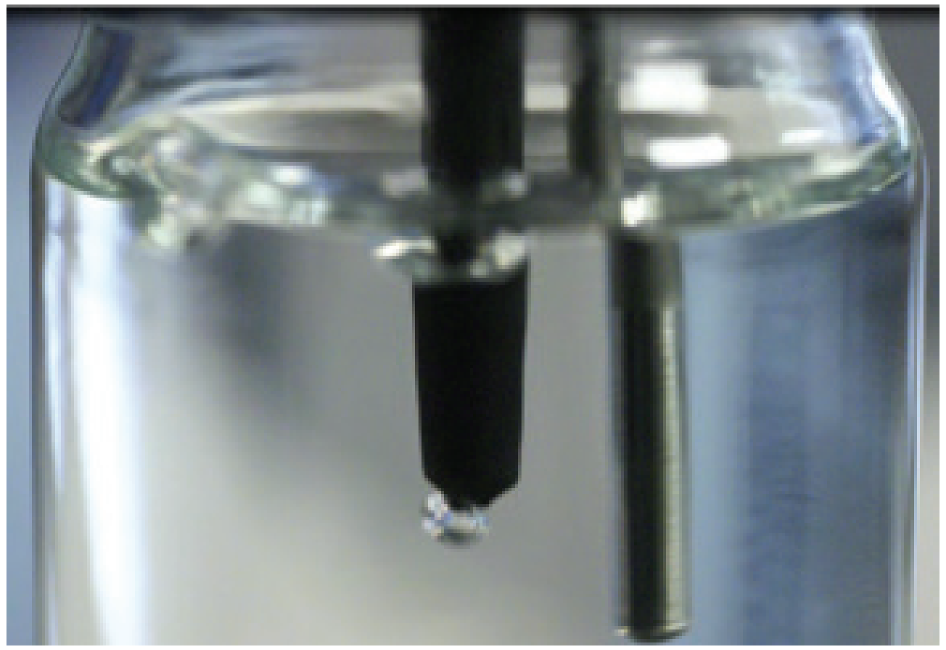
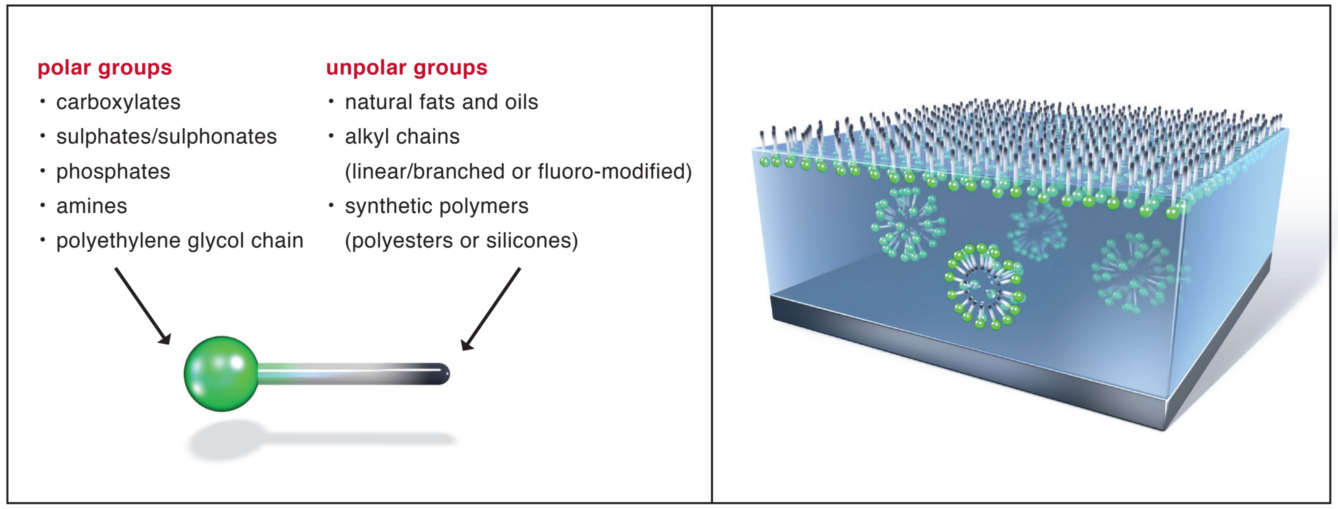


Figure 3:
Bubble pressure tensiometer producing a gas bubble in a liquid

Surface tension is influenced by surfactants or surfactant-like molecules. The term surfactant comes from "surface active agent". Surfactants (or surfactant-like molecules) are interfacially active. They have a strong tendency to migrate to and to accumulate at interfaces. There they lower the surface tension (or interfacial tension) between two phases. In that way surfactants may act as detergents, wetting agents, emulsifiers, foaming agents and dispersants.

Unfortunately, surface tension measurements in pure water reveal little about the behaviour of wetting agents in real coating formulations. It is therefore important to additionally check the effect of wetting agents in the final coating or, at least, relevant binders.

From a chemical point of view surfactants are usually organic compounds that are amphiphilic, meaning they contain both polar and unpolar groups in one molecule. For aqueous systems, a surfactant usually contains both a water-insoluble (hydrophobic) group and a water-soluble (hydrophilic) group. Due to the insoluble hydrophobic part, acting as a low surface tension component, the surfactant molecule has a tendency to migrate to the air/water interface or be absorbed at other hydrophobic surfaces (e.g. oil droplets). At the air/water interface the water-insoluble hydrophobic groups extend out of the bulk water phase and into the air, thus lowering the surface tension of the water.



polar groups
- carboxylates
- sulphates/sulphonates
- phosphates
- amines
- polyethylene glycol chain

unpolar groups
- natural fats and oils
- alkyl chains (linear/branched or fluoro-modified)
- synthetic polymers (polyesters or silicones)

Figure 4:
Surfactants arrange at the air/liquid interface and in the form of micelles in the liquid

In a broader sense this surfactant effect is also true for solvent-based systems. Here, rather un-polar groups (e.g. silicones or fluorinated side chains) are combined with more polar structures (e.g. polyesters, polyacrylates). Also, the unpolar groups have a tendency to migrate and accumulate at the air/solvent interface, resulting in a reduction of the surface tension.

Wetting Agents and Surface Modifiers: Background

Substrate Wetting

Surface defects often occur during or after the coating application. These defects degrade both the optical properties of the coating and its ability to protect the substrate. Formulating a defect-free coating can be achieved by controlling the surface chemistry of the coating. More specifically, local surface tension differences are the actual cause of many surface defects. These local differences can be compensated by the use of substrate wetting agents.

Substrate wetting depends primarily on the surface tension of the paint and on the surface tension of the substrate to be coated. As a general rule, wetting takes place if the surface tension of the liquid is lower than the surface energy of the substrate's surface. This criterion for wetting is also known as the wetting condition and is illustrated in Figure 5. Poor wetting (such as “de-wetting”) will occur if the surface tension of the paint is higher than the surface tension of the substrate.

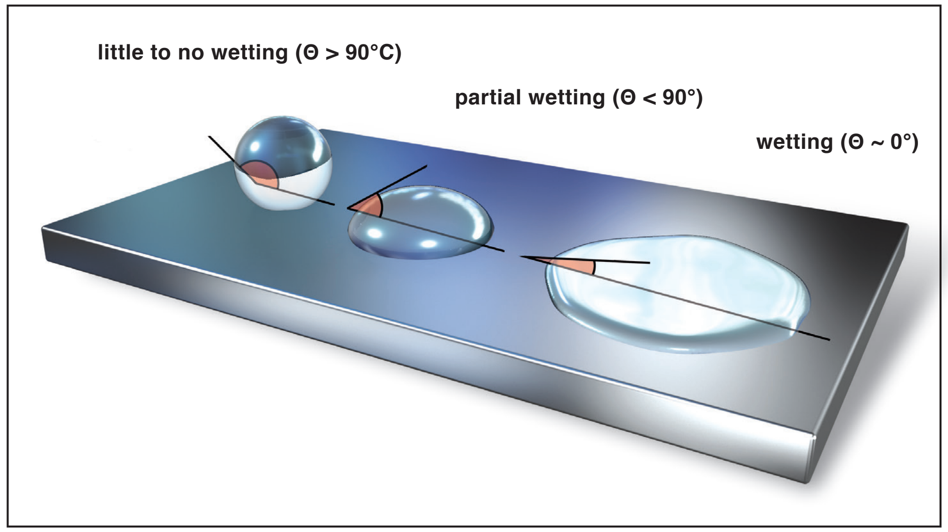


Figure 5:
Three wetting conditions and their relation to contact angles

As shown in Table 1 substrates with low surface tensions are not easy to wet with water. Special substrate wetting agents are required to lower the surface tension and enable sufficient substrate wetting. Therefore, an effective wetting agent for a coating formulation should have surfactant characteristics in order to lower the surface tension of the liquid to allow the liquid to wet the surface. This is especially of importance if hydrophobic substrates (e.g. plastics) have to be coated with aqueous formulations.

It should not be underestimated that diffusion and adsorption of surfactants at interfaces is a time-dependent process. New interfaces are produced extremely fast during spraying, printing or coating. The mobility of the surfactants is thus an important factor.

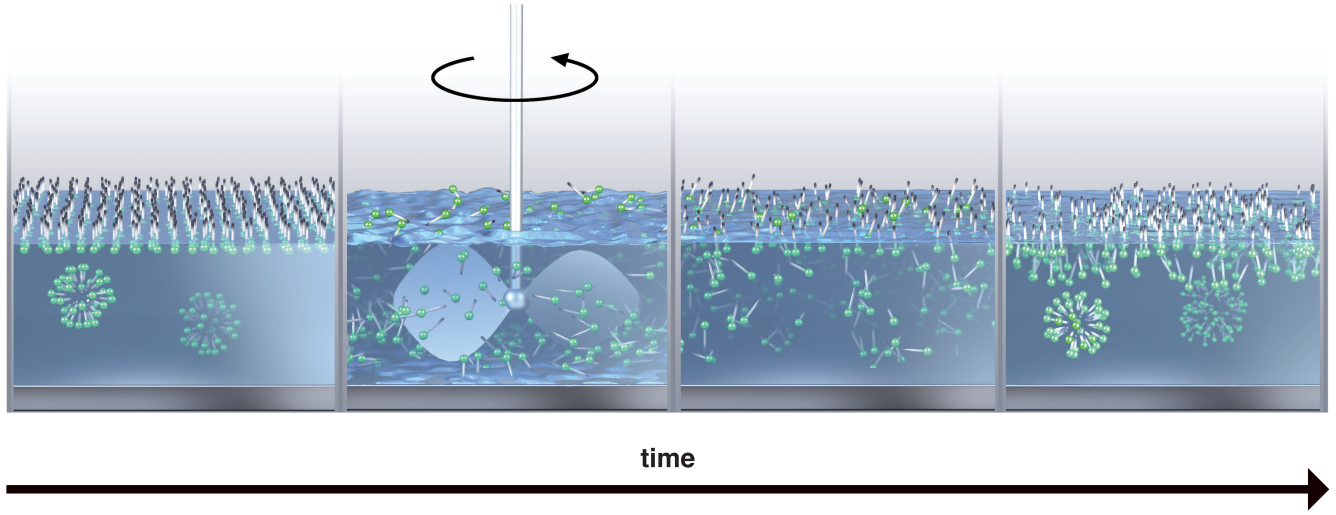


Figure 6:
Schematic representation of the dynamic behavior of surfactants. After formation of new surfaces (stirring), surfactants need some time to migrate to the newly formed interfaces and to lower the surface tension again

For fast processes it is recommended to use highly dynamic surfactants, which ensure low surface tension even if new surfaces are formed very quickly. The dynamic behavior of wetting agents is illustrated in Figure 6.

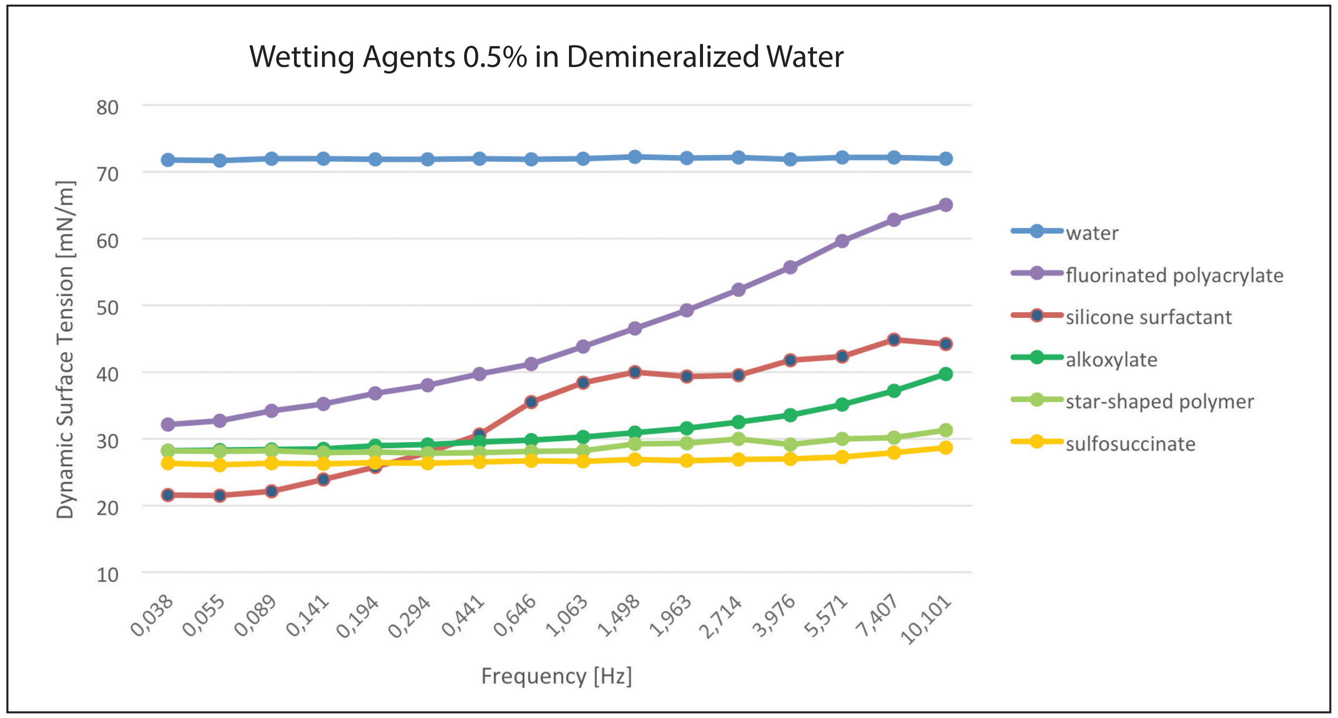


Figure 7: Dynamic surface tension at different bubble frequencies of various wetting agents in water

The ability to lower the surface tension even under highly dynamic conditions (high bubble frequency) depends on the mobility of the surfactants. Sulfosuccinates and alkoxylated surfactants can cover newly formed interfaces rather quickly. Whereas the fluorinated polyacrylates and the silicone surfactants are slower due to their higher molecular weight and different aggregation behavior.

Wetting Agents and Surface Modifiers: Background

Anti-Cratering

The reasons for crater formation can be various. Craters can be formed due to contamination with low surface tension materials that are not compatible with the coating system. The system will de-wet from a low surface tension material and create a crater or a fish eye. Craters can originate from uncleaned or contaminated substrates (e.g. oil droplets). Additionally, they can be caused by overspray falling onto a freshly sprayed paint film.

To solve crater problems, the surface tension of the system should be lowered with proper wetting agents in order to allow the system to wet the contaminating material.

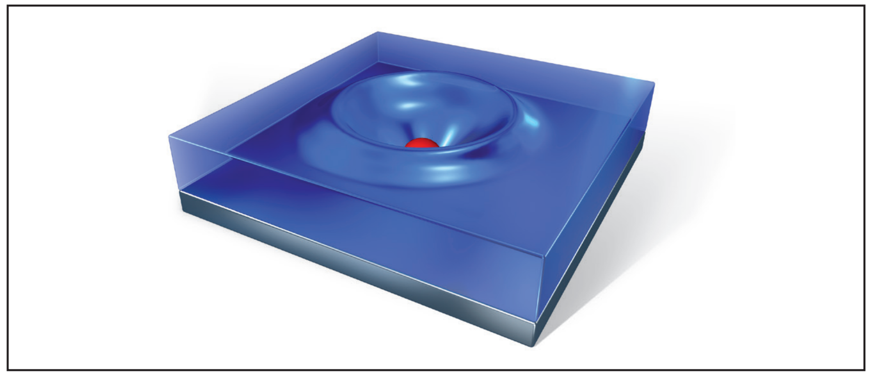


Figure 8:
Schematic representation of a crater with a particle in the center. The liquid coating is receding from the particle due to surface tension differences

Pin Holes

Pin holes are channels resulting from slow rising micro air bubbles that are unable to separate from the substrate. A pin hole does not contain contamination with low surface tension material. This is the fundamental difference to craters.

The major issue with pin holes is that they are entry channels for corrosion. In order to avoid pin holes the right combination of defoamer and wetting agent is required. Micro air bubbles should be avoided by using a proper defoamer. And a complete substrate wetting should be supported through the use of a low-foaming wetting agent.

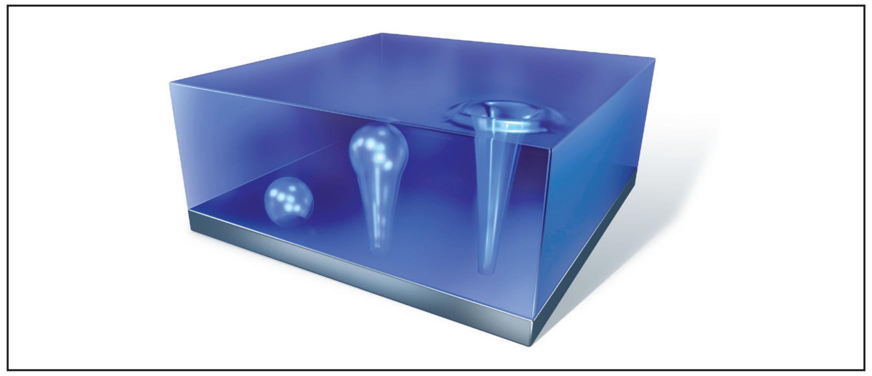


Figure 9:
Schematic illustration of pin hole formation

Leveling

Leveling is defined as the ability of a coating to flow out after application in order to obliterate any surface irregularities such as brush marks, orange peels or craters.

Good to know

Orange peel is a surface bumpiness or waviness that resembles orange skin which is often caused by poor leveling.

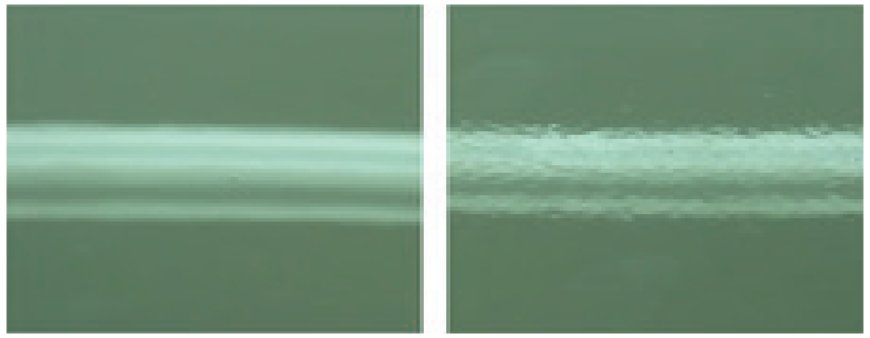
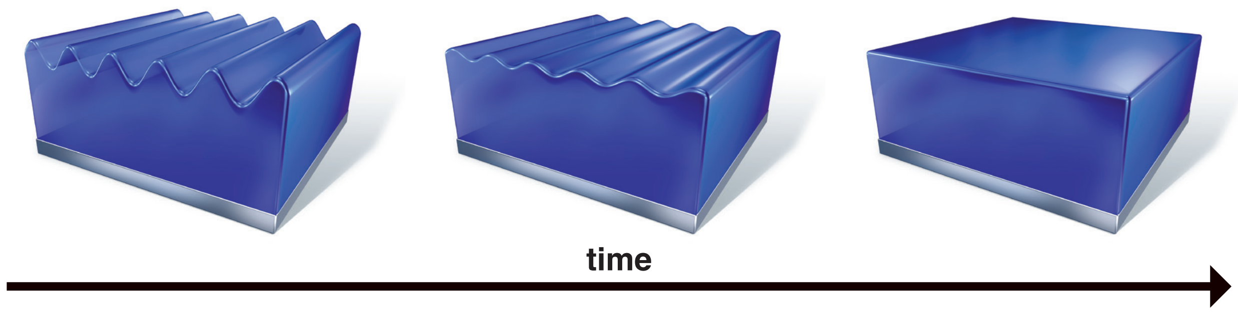


Figure 10: Good and bad leveling (“orange peel”)



$$t = G\frac{\eta}{\gamma d^{3}}$$

t : time needed for leveling
γ: surface tension of liquid
G : specific constant
d : film thickness
η: viscosity of liquid

Figure 11: Leveling equation for a Newtonian liquid

Wetting Agents and Surface Modifiers: Background

As described in Figure 11, leveling is a time-dependent phenomenon. The leveling time (t) is directly proportional to the viscosity (η) of the liquid. It is reciprocally proportional to the surface tension (γ) and to the third power of the film thickness (d). If a coating is applied at a different film thickness, it will need different time spans to achieve a final flat surface. For example, if the film thickness is doubled it will decrease the leveling time by a factor of eight.

On the other hand, good leveling is critically important for especially thin, fast drying coatings (e.g. can or coil coatings). In can and coil coatings the time allowed for leveling is very short, the film thickness is given and the viscosity of the system is also not easy to change. Therefore, the only factor that can be manipulated easily is the surface tension of the system.

The equation in Figure 11 conveys the impression that a high surface tension supports good leveling. In many cases it seems that a lower surface tension improves the leveling.

To understand this contradiction we have to realize that the surface of a liquid coating (especially during drying) is not homogeneous on a microscopic level. The surface tension can be locally very different as shown in Figure 12.

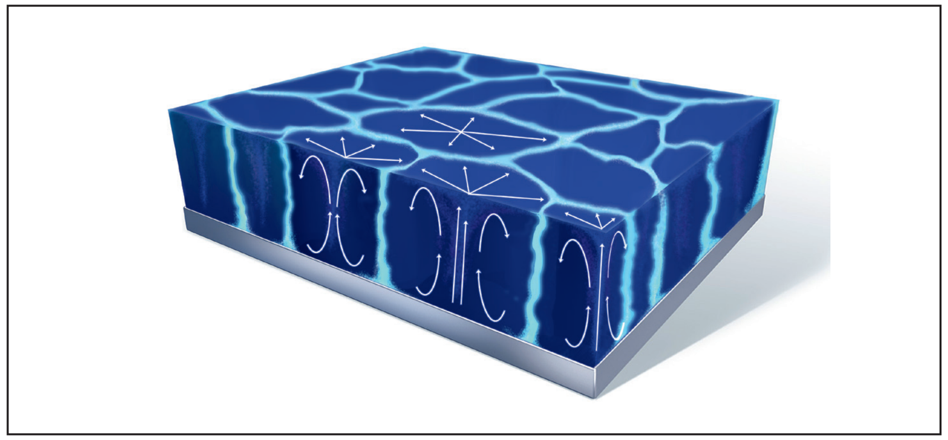


Figure 12:
When drying, the surface tension of a coating can be locally very different (surface tension gradient). Turbulence inside the liquid coating leads to areas with higher and lower surface tension

Adding a surfactant to the system will lower the overall surface tension on a microscopic level. It will also equalize local surface tension differences, resulting in improved leveling and smoother surfaces. In the case of coil coating applications a true surface tension balance is needed to achieve good leveling. Experience shows that fluorocarbon-modified polyacrylates are the most suitable products here. They lower the surface tension to overcome possible defects but not too low to cause bad leveling.

Slip

A slip agent acts as an internal lubricant by migrating to the surface of the coating to reduce friction and improve slip. In many cases it is not only slip itself, but rather the addition of slip properties with other features of a coating that are of prime interest. Surfaces with higher slip are more scratch resistant, less easily soiled, easier to clean and more resistant to blocking.

Often organomodified silicone additives are used to improve the surface slip properties of coatings. Their chemical structure controls the degree of surface slip increase. Basically, products with a higher silicone content and higher molecular weight provide higher slip, whereas products with less dense and shorter chain silicone structures provide significantly less slip improvement.

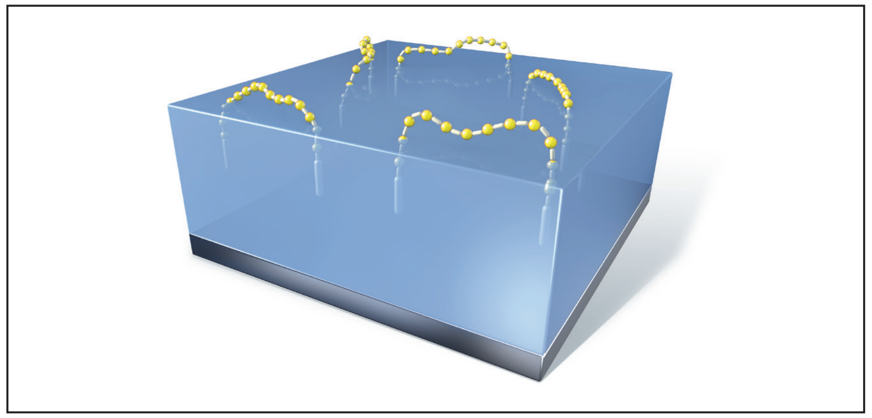


Figure 13:
Orientation of organomodified silicones at the surface of a coating. Silicone chains (yellow) orient themselves at the liquid/air interface, whereas the organic side chains have a good compatibility with the coating matrix

Some formulators are hesitant to use additives containing silicone due to the fact that silicone has an unjustified reputation for causing problems in regard to recoatability and intercoat adhesion. A proper choice of organo-modified silicone additives and dosage can avoid many problems in this respect.

There are at least two conditions that can influence intercoat adhesion or overcoatability:
(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 additive level. Higher dosage levels do not necessarily provide additional advantages (wetting, anticrater effect, slip, etc.) but may cause undesirable side effects such as loss of intercoat adhesion.

Another important factor is the curing temperature. Polyether modifications on organomodified silicones start to decompose at temperatures of about 140-150°C. A product of this decomposition process can be unmodified silicone oil which might have a negative influence on intercoat adhesion. For higher temperature applications it is recommended to use other organomodified silicones (e.g. alkyl modified silicones).

Good to know

Slip agents also provide or improve mar and block resistance of a coating.

Mar resistance is the ability of a coating to resist damage caused by light abrasion, impact or pressure (e.g. scratches or metal marking).

Block resistance is the capability of a coating, when applied to two surfaces, not to stick to itself upon contact when pressure is applied.

Wetting agents and surface modifiers product range

Wetting agents and surface modifiers product range

BASF Formulation Additives offers a broad portfolio of wetting agents and surface modifiers for water-based and solvent-based systems based on various chemistries.

Chemistry	Product Range	Characteristics
Alkoxylated surfactant	Hydropalat®	Low foaming substrate wetting agents for waterborne applications
Silicone surfactants	Efka® Hydropalat®	Substrate wetting agents with generally very low static surface tension
Sulfosuccinates	Hydropalat®	Cost effective substrate wetting agents with excellent dynamic surface tension reduction
(Fluorinated) polyacrylates	Efka® Hydropalat®	High-performance acrylate leveling agents for waterborne and solvent-based borne applications
Star-shaped polymers	Hydropalat®	Defoaming wetting agents based on star-shaped polymers for excellent dynamic surface tension reduction

Wetting Agents and Surface Modifiers: Background

Sulfosuccinates

Sulfosuccinates are highly dynamic, cost-effective wetting agents. Their excellent dynamic surface tension reduction qualities and broad food contact compliance makes them commonly used substrate wetting agents in the printing and packaging industry.
Sulfosuccinates are also known to be foam stabilizing. Due to their excellent wetting capability, they are also used as compatiblizer (color acceptance agents) in architectural paints.

Alkoxylated Surfactants

Alkoxylated surfactants are usually cost-effective, non-ionic wetting agents. Depending on the starting alcohol, the ratio of ethylene oxide to propylene oxide and the overall degree of alkoxylation, their hydrophilic-lipophilic balance (HLB) can vary widely. Some alkoxylated surfactants are especially low-foaming wetting agents.

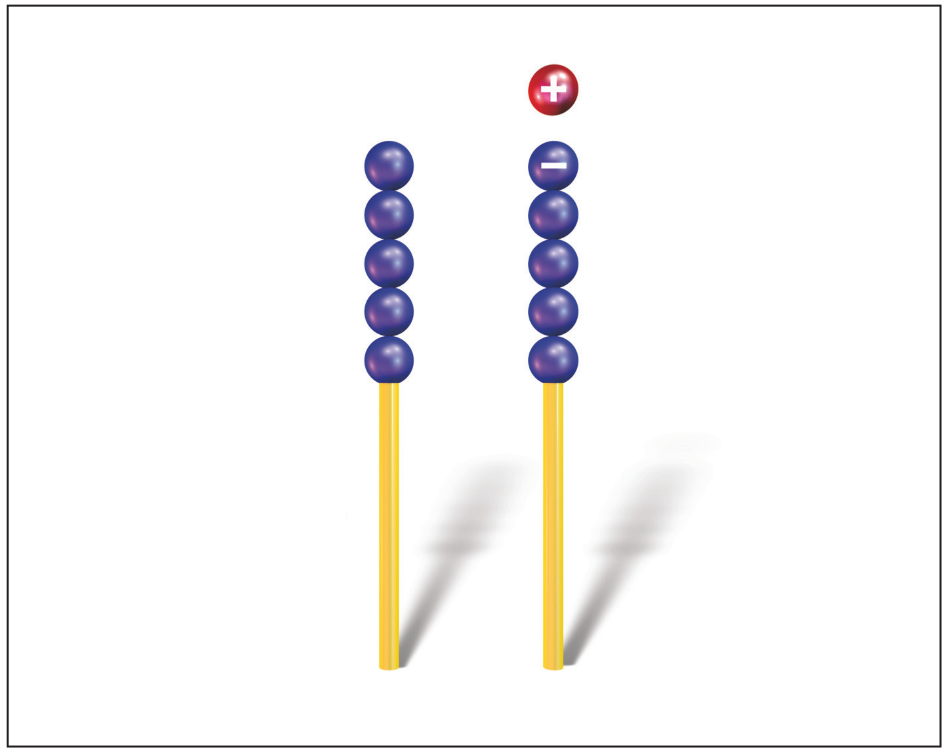


Figure 14:
Schematic representation of surfactant-type low molecular weight dispersants

Star-shaped Polymers

A very special class of alkoxylated surfactants are star-shaped polymers (former Starfactant®). The hyper-branched structure of these non-ionic surfactants was modified to give them additional wetting and defoaming properties. The chemistry is based on standard raw materials like fatty alcohol ethoxylates.

They are non-ionic wetting agents that are virtually 100 percent active and designed for the use in waterborne coatings for metals, woods and plastics. These liquid products are free of silicones and alkylphenol ethoxylates and are not formulated with additional solvents.

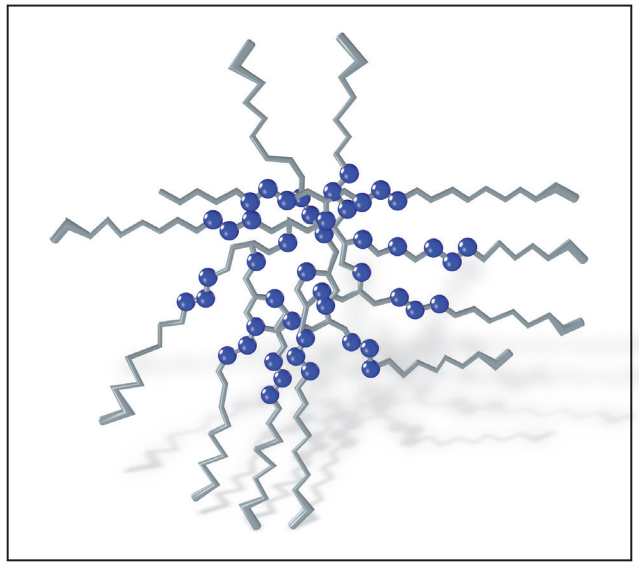


Figure 15:
General chemical structure of star-shaped polymers

Organomodified Silicones

Organomodified silicones are a very versatile class of polymers. Depending on the degree of modification and the overall silicone oil content they can be employed as substrate wetting agents, flow and leveling agents and/or slip agents.

In general, silicone-based additives reduce the surface tension of a formulation rather drastically. Silicones are very surface-active polymers that provide low surface tension and they always try to orientate themselves on the air/liquid interface. This makes them ideal raw materials for interfacially active additives. Silicone surfactants, due to their short chain lengths will not provide surface slip in most paint systems.

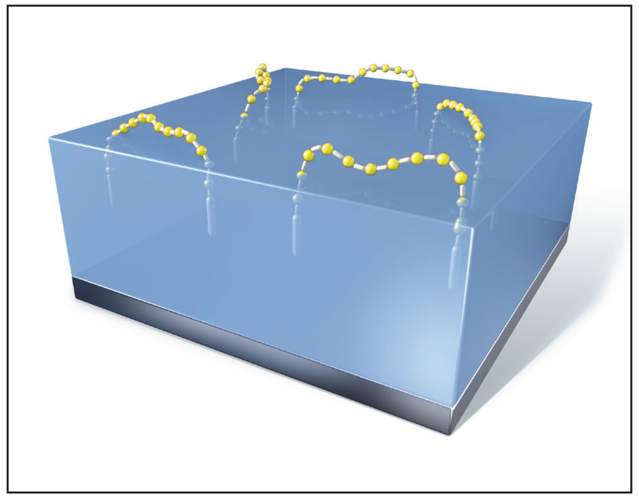


Figure 16:
Example of orientation of alpha-omega organomodified silicones at the surface of a coating. Silicone chains (yellow) orient themselves at the liquid/air interface, whereas the organic side chains have a good compatibility with the coating matrix

Wetting Agents and Surface Modifiers: Background

(Fluorinated) Polyacrylates

Also (fluorinated) polyacrylates are a very versatile class of interfacially active additives. They are widely used in the coating industry as flow and leveling agents.

Pure polyacrylate copolymers are highly appreciated for their flow performance, although they do not significantly reduce the surface tension of a formulation. Pure polyacrylate copolymers homogenize local surface tension differences (see Figure 12). The surface tension gradient is the decisive factor here. The additives homogenize the surface tension gradients to achieve a real flat surface of the coating.

Polyacrylates do not significantly lower the surface tension of a system, which means that they are not so much interfacially active. Their influence on intercoat adhesion is therefore negligible.

A straight polyacrylate cannot solve problems like cratering, poor substrate wetting and other problems related to surface tension. Fluorinated polyacrylates have been developed as a result. These polyacrylates with fluorinated side chains can lower the surface tension of a formulation. They combine excellent flow and leveling with anti-cratering and good wetting behavior.

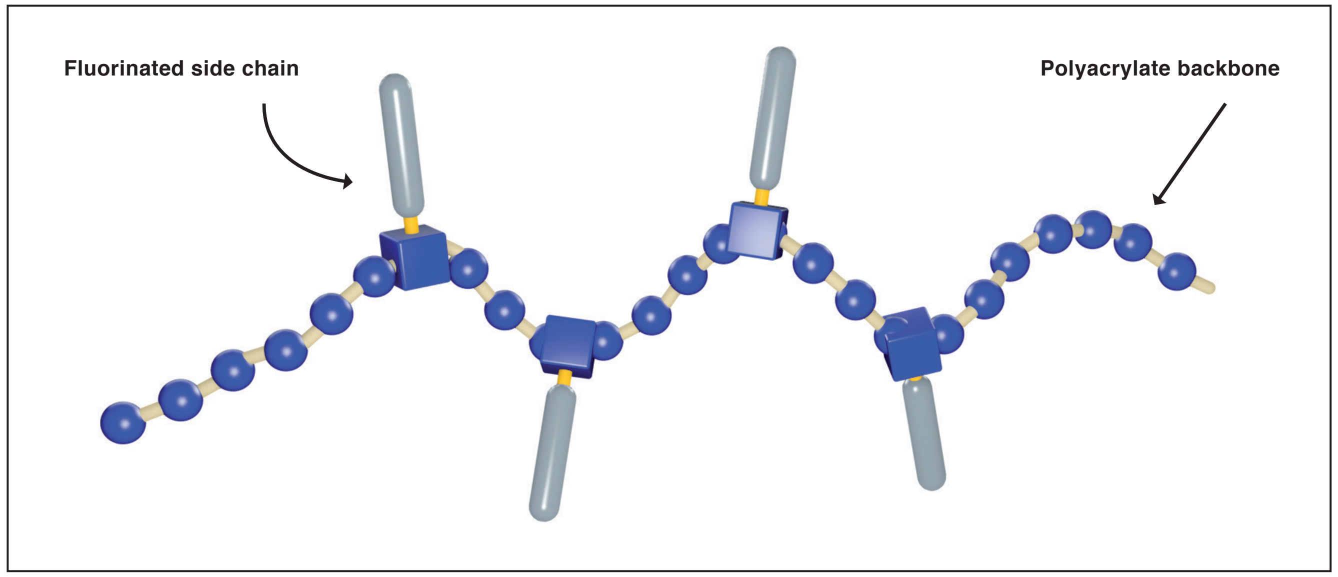


Figure 17:
General chemical structure of a fluorocarbon-modified polyacrylate

Properties	Polysiloxane	Polyacrylate	Fluorocarbon-Modified Polyacrylate
Slip	Very high	None	None
Leveling	Excellent	Good	Good
Flow	Good	Excellent	Excellent
Surface tension reduction	Excellent	Moderate	Excellent
Anti Crater	Excellent	Little	Excellent
Anti fish eye	Good	Average	Excellent
Substrate wetting	Good	Average	Excellent
Anti Bernard Cells	Excellent	None	Good
Possibility for Intercoat Adhesion problem	Yes	No	No
Foam stabilization	High possibility	No	Low

Table 2:
Comparison of the properties of organomodified polysiloxanes, straight polyacrylates and fluorinated polyacrylates.

In comparison to organomodified silicones and straight polyacrylates, fluorocarbon-modified polyacrylates have clear advantages with respect to flow, substrate wetting and fish-eye resistance. On the other hand, polysiloxanes can provide strong surface slip and anti-blocking effects and reduce surface tension.

The newest generation of fluorinated acrylates are block copolymers with fluorinated side chains. These unique products are made via controlled free radical polymerization (CFRP), which allows the synthesis of block copolymer structures and to concentrate the fluorinated side chains in one polymer block only.

Such an arrangement makes best use of the fluorinated side chains and guarantees maximum effectiveness with respect to substrate wetting and anti-cratering behaviour.

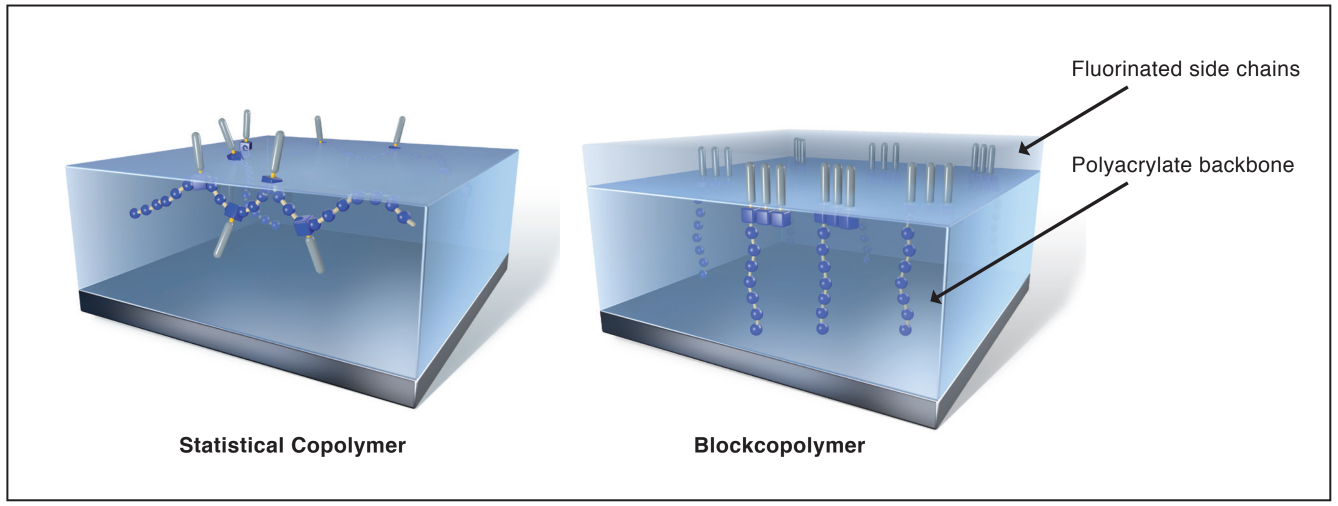


Figure 18:
Illustration of a fluorinated polyacrylate at the liquid/air interface. The block copolymer arrangement makes maximum use of the fluorinated side chains