![BYK Additives & Instruments]

Wetting and Dispersing Additives

Welcome to the interactive world of BYK additives. This multimedia "wetting and dispersing additives" brochure has been designed to support your work, offering interactive graphics fascinating animations and videos to show the chemical processes.

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01
Why do we use 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. If this pigment grinding step is not optimized, a wide variety of defects can occur:

Flocculation
Gloss reduction
Color shift
Separation,
formation of Bénard cells
Settling.

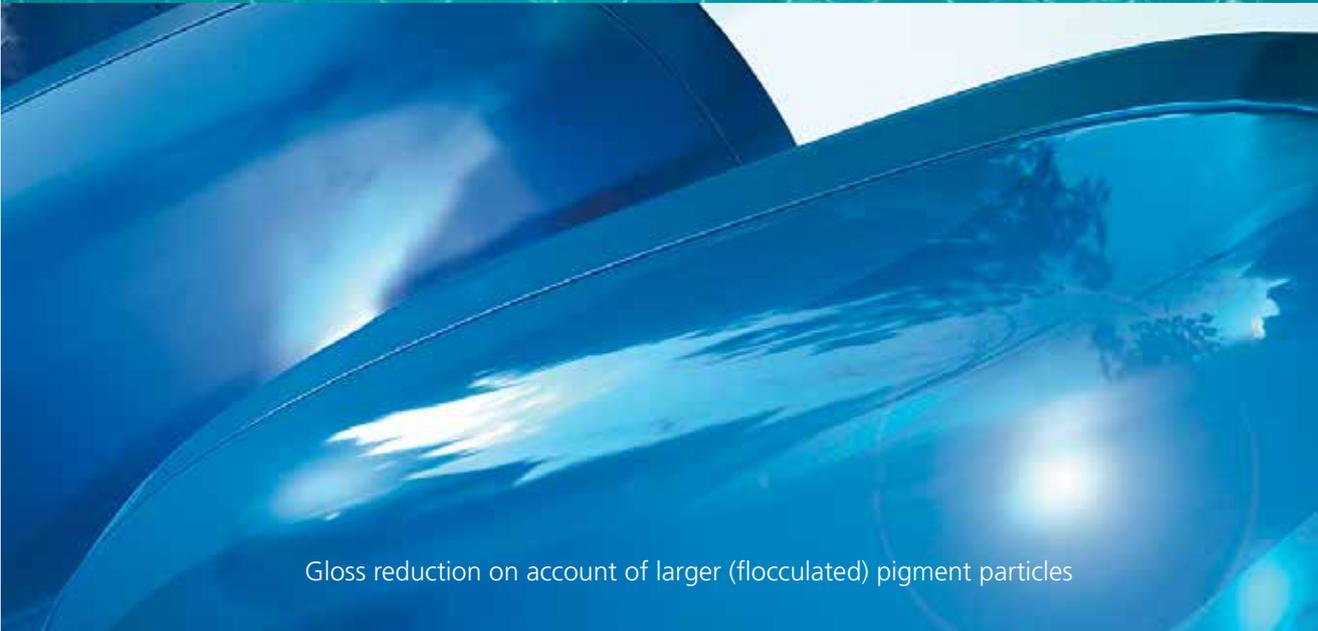Properties related to the flow characteristics of the coating system, such as
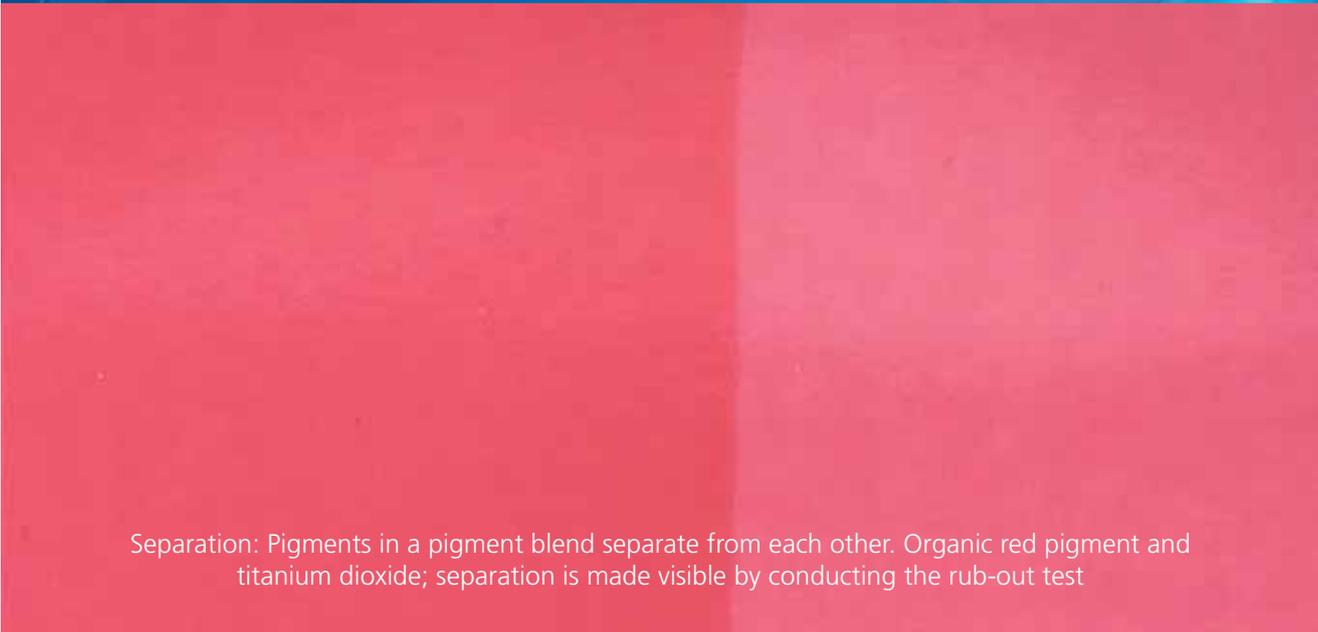
Sagging
Leveling

can also be negatively affected.

Possible paint defects...

Phthalocyanine blue and titanium dioxide; formation of Bénard cells

Gloss reduction on account of larger (flocculated) pigment particles

Separation: Pigments in a pigment blend separate from each other. Organic red pigment and titanium dioxide; separation is made visible by conducting the rub-out test
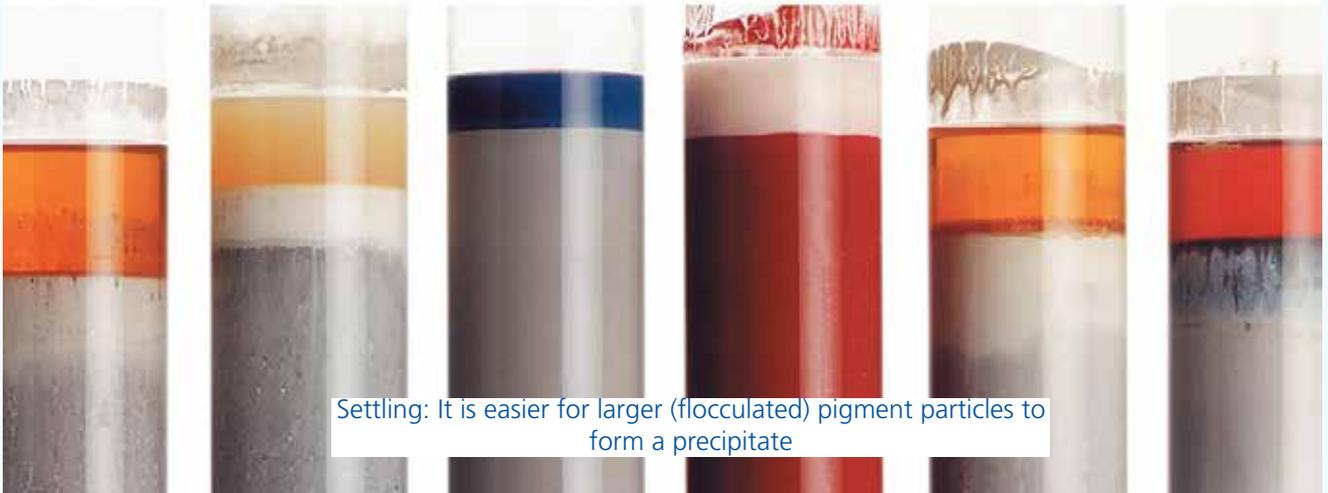
Settling: It is easier for larger (flocculated) pigment particles to form a precipitate
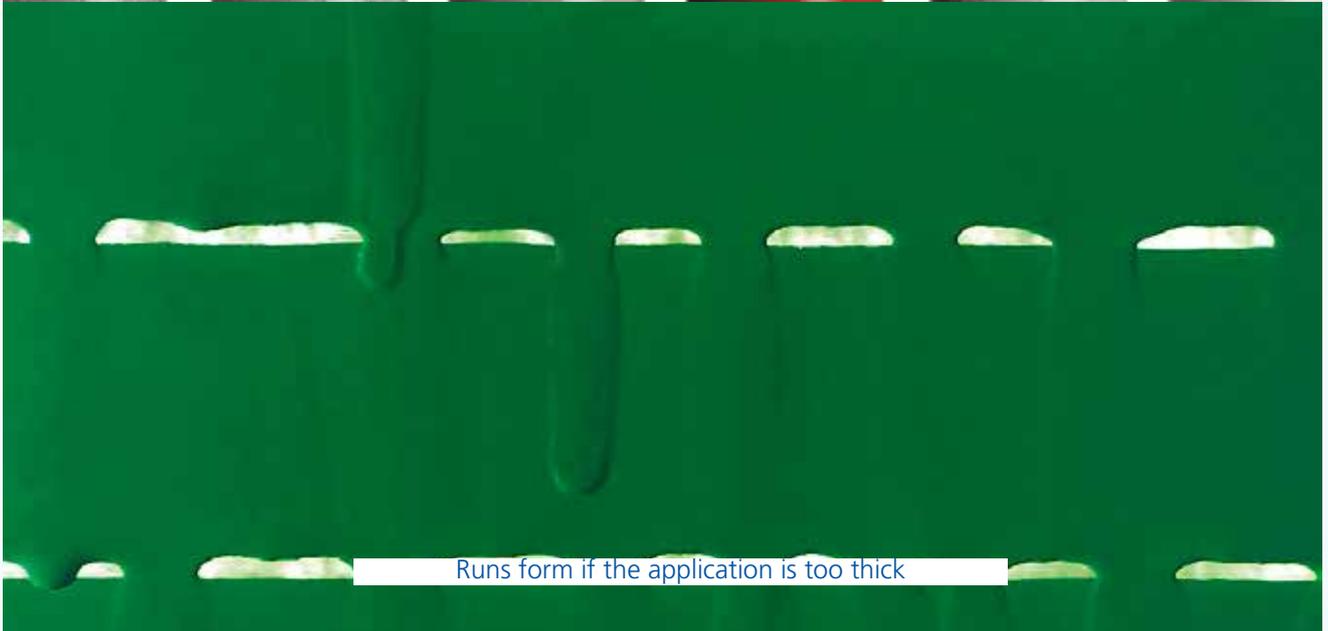
Runs form if the application is too thick

Runs form if the application is too thick

Poor leveling

Flocculation: Individual pigment particles come together to form larger structures

02
Pigment dispersion

Pigments are usually incorporated in the coating in the form of dry pigment powders. The pigments are not primary particles, they are agglomerates. **Agglomerates** represent pigment "groupings" in which the spaces between the individual pigment particles contain air and moisture. These individual pigment particles are in contac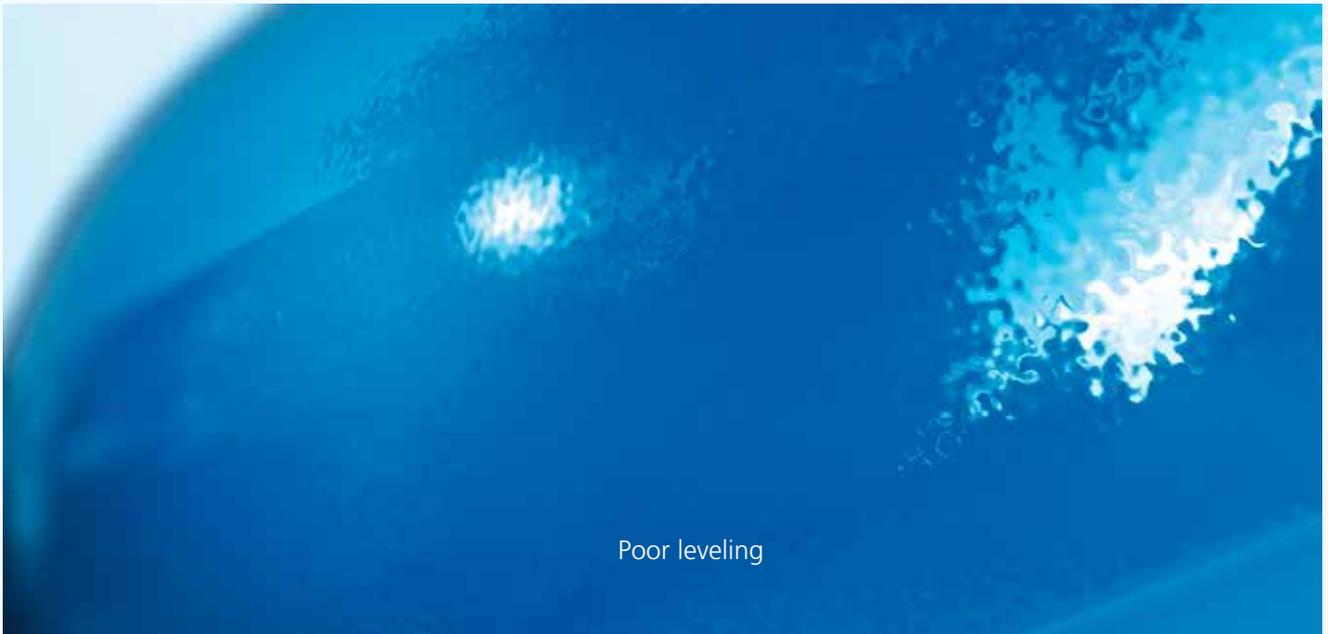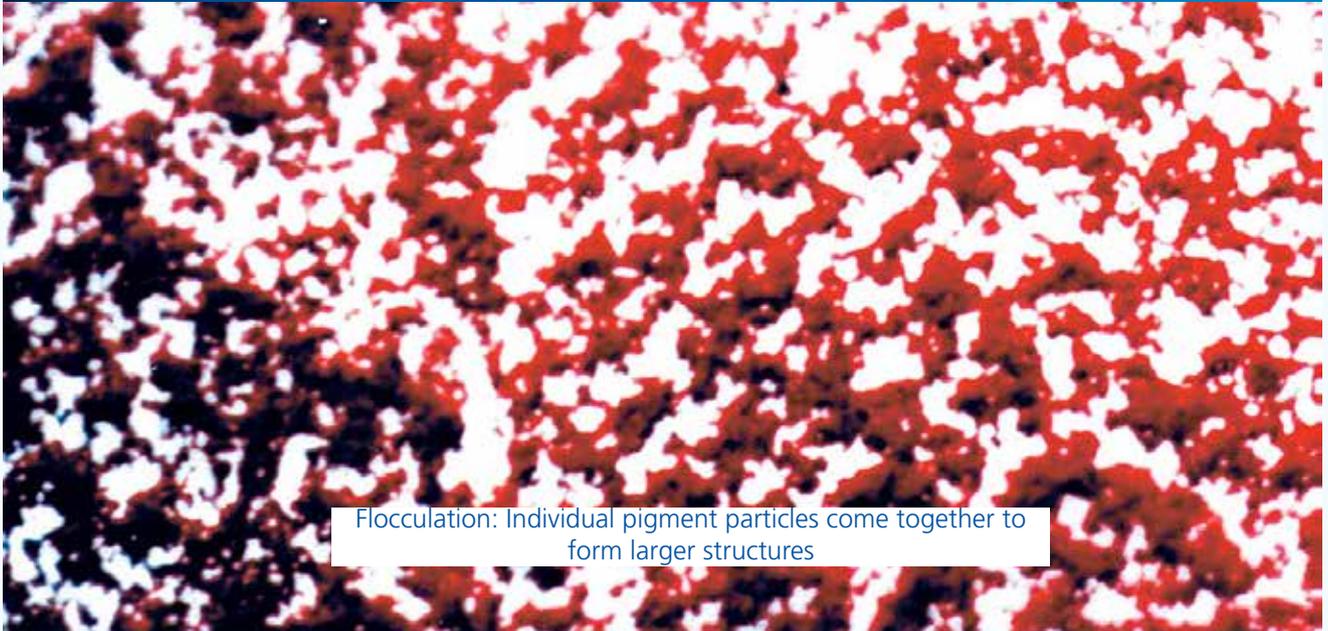t with one another only along their edges and corners. Interactive forces between the particles are relatively small so that such forces can be overcome by traditional dispersing units. In the case of pigment dispersion, the pigment agglomerates are broken up by impact and shearing forces, which ideally lead to **primary particles**.

During this process, energy is supplied to the coating system and therefore smaller particles are formed, with a larger interface to the resin solution. The system then endeavors to escape this energy-rich state in order to revert to its previous low-energy state: the finely distributed pigments come back together to form larger structures which are then known as flocculates. This is expressed, for example, by the reduced color strength, decreased gloss, and altered rheology. In terms of structure, the **flocculates** are very similar to the agglomerates; nevertheless, the interstitial spaces between the pigments are now filled with a binder solution rather than air.

Pigment dispersion and flocculation

Agglomerate

Flocculated condition

Primary particles

Deflocculated condition
Ideal dispersion
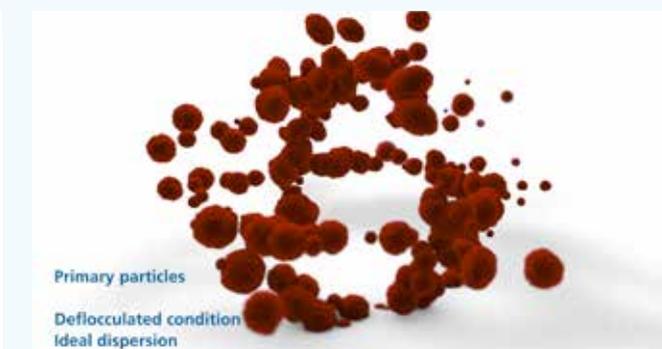
Flocculation/deflocculation: two droplets of paint (organic red pigment) under the microscope

Without wetting and dispersing additive: Strong flocculation

With wetting and dispersing additive: Perfect dispersion, no flocculation

Flocculation/deflocculation: two dispersions of a fine-particle carbon black pigment in transmitted light

Without wetting and dispersing additive

With wetting and dispersing additive

Strong flocculation

Perfect dispersion, no flocculation

03
The dispersion process

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

During **Step 1**, all of the air and moisture at the pigment surface is displaced and then replaced by the binder solution. The binder solution wets the pigment particles and the solid/gaseous interface (pigment/air) is transformed into a solid/liquid interface (pigment/binder solution). To do this, the binder solution must penetrate into the interstitial spaces of the agglomerate.

Step 2 represents the actual **dispersing** of the pigment. Through mechanical energy (impact and shear forces), the pigment agglomerates are broken up and accordingly reduced to their particle size.

In the concluding **Step 3**, the pigment dispersion must be **stabilized** in order to prevent the formation of uncontrolled flocculation. As described later in more detail, suitable measures are used to keep the individual pigment particles at appropriate distances from one another so that they cannot congregate. In most applications the stabilization of the deflocculated state is desirable; in some applications the pigment dispersion can also, however, be stabilized by controlled flocculation (which will be discussed later).

Steps 1 (wetting) and 3 (stabilizing) can be optimized by additives. **Wetting additives** accelerate the wetting of the pigment agglomerates using the binder. **Dispersion additives** improve the stabilization of the pigment dispersion. One and the same product can often function as both the wetting and the dispersing additive.

Additives will not help in step 2, the actual dispersion of the pigment agglomerates, even if the term "dispersion" additive would suggest the contrary. Here it is important that the mechanical forces are great enough to break up the agglomerates and that the dwell time of the agglomerates in the sphere of action of these forces is of sufficient length. If the agglomerates are broken up as much as possible, the dispersing additives can then stabilize this state and effectively suppress flocculation.
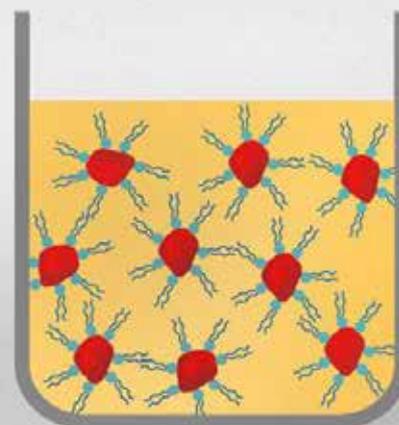

1 Wetting   2 Dispersing   3 Stabilizing
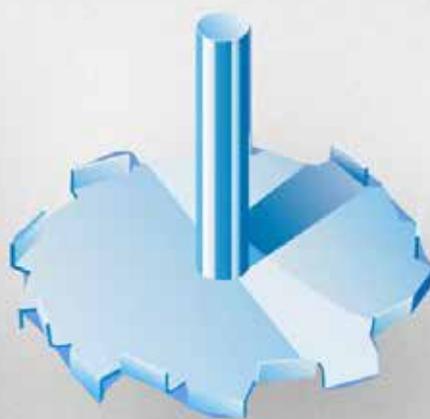
04
Wetting additives

The wetting of the pigment agglomerates through the binder solution is influenced by many factors. The penetration speed of the liquid phase into the interstices of the agglomerates is – under considerably simplified conditions – mathematically expressed by the **Washburn equation**.

$$v = \frac{dl}{dt} = \frac{r}{2l\eta} \cdot \gamma \cos\Theta$$

v = Penetration speed	t = Time	η = Viscosity of the liquid phase	Θ = Contact angle
l = Penetration depth	r = Capillary radius	γ = Surface tension of the liquid phase	

The capillaries between the pigment particles are assumed to be cylindrical tubes with radius r. The first factor on the right hand side of the equation shows that for fast wetting (high penetration speed) loosely packed agglomerates (r is large) and a low viscosity are favorable. However, the agglomerate structure cannot be influenced by the coating producer and the possibilities for viscosity reduction are fairly limited.

The second factor looks more promising: here we have the surface tension of the penetrating liquid and the contact angle. Both can be influenced by **wetting additives** but they are not independent from each other: it is not possible to have a high surface tension together with a low contact angle. In practice, wetting additives are used to lower the surface tension as far as necessary to bring the contact angle close to zero; lower surface tension values should be avoided.

Wetting additives can be defined as substances which are designed to reduce the contact angle between the pigment and binder solution and which, as a result, accelerate the penetration speed of the liquid into the agglomerate structure. Characteristic for such substances is their **surfactant structure**: polar, hydrophilic structural elements along with non-polar, hydrophobic structural elements are combined in one molecule. Because of this very structure, such compounds are interface-active, i.e. the wetting additives migrate to the pigment/binder solution interface. From a chemical perspective, wetting additives can be classified as either ionic or non-ionic – according to how the polar segment is incorporated into the molecule. The non-polar segment is, as a rule, represented by hydrocarbon chains.

Pigment wetting

No wetting

BYK

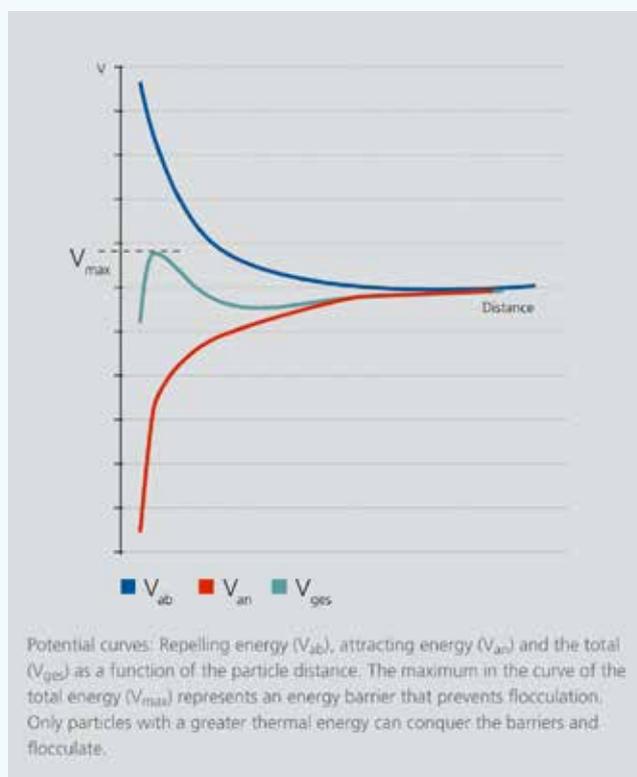Addition of
wetting additive

Immediate wetting

BYK

05
Dispersing additives

Dispersing additives are needed to **stabilize** the state achieved after the pigment grinding (fine distribution of the pigment particles in the binder solution) for a long period of time, i.e. to prevent the flocculation of the pigments.

Flocculation is caused by the attractive London-van der Waal forces occurring between the particles. These forces are effective only across a small distance, but the Brownian molecular motion causes the particles to collide time and again or at least causes them to become too close to each other and therefore creates flocculation.

In order to stabilize a system against flocculation, repelling forces must be used between the particles. The interaction of the attracting and repelling energies between the particles is usually represented in the form of potential curves. The total of both curves results in the total energy.

Potential curves: Repelling energy (V_{ab}), attracting energy (V_{an}) and the total (V_{ges}) as a function of the particle distance. The maximum in the curve of the total energy (V_{max}) represents an energy barrier that prevents flocculation. Only particles with a greater thermal energy can conquer the barriers and flocculate.

Dispersing additives adsorb on the pigment surface and bring about considerable repelling forces between the pigment particles. This keeps the particles at a distance and reduces the tendency towards uncontrolled flocculation. In practice, this takes place by means of **electrostatic repulsion** and/or **steric stabilization**. Both stabilization measures are described below.

Deflocculation generates rather Newtonian flow characteristics along with generally reduced viscosity. This, in turn, improves leveling behavior and enables higher pigment loading.

Due to the small particle size of the deflocculated pigments, high gloss is obtained and color strength is increased. Likewise, transparency or opacity is increased, dependent upon whether the respective pigment was designed by the manufacturer to be transparent or opaque. Deflocculation leads in general to an improved, more efficient pigment utilization, which (especially in the case of the sometimes rather expensive organic pigments) is of economic significance.

The flocculation level also has an influence on the color of a pigment: if, for example, a system tends to flocculate upon storage, then color change can result. In situations where this is especially critical (such as in the base component of a mixing system or with very high-quality coating systems), the only way to produce coatings with a constant and defined color is through complete deflocculation. Generally speaking, a good deflocculation of all pigments is extremely beneficial and desirable for all pigmented topcoat systems.

06
Electrostatic stabilization

The dissociated ionic structures in the solid surface and selective ion adsorption cause dispersed solid particles in a liquid phase to carry **electric charge**. As the entire system is electrically neutral, the appropriate number of counter ions must be present in the adjacent liquid. We talk about an electrical double layer, which is made up of an adsorptive bound layer and a diffuse layer, in accordance with Stern's model.

When two particles get close to one another, the double layers influence each other; in the case of opposite electrical charge they are attracted to each other, and with like charges they repel each other. The interaction between these electrostatic forces and the attracting London-van der Waal forces are described by the DLVO theory.

Additives can significantly influence the **surface charge** of the pigment particle: a targeted generation of strong charges brings about a high **repulsion potential** and thereby suppresses flocculation. **Polyelectrolytes** are particularly suitable as dispersing additives which function in this manner. Their polymer structure enables them to be readily and sustainably adsorbed on the pigment surface, and their multitude of ionic groups brings about considerable surface charges.

This type of stabilization is basically restricted to **aqueous systems**, as only here (on account of the high dielectric constant of the water) can sufficiently strong charges be produced. In principle, this mechanism also functions in organic solvents, however the surface charges are much lower, i.e. the thickness of the electrical double layer is considerably reduced and not usually sufficient to effectively prevent flocculation in the majority of cases.

Alongside the dielectric constant, the ion concentration and, above all, the valency of the ions have a strong influence on the electrical double layer. High ion concentrations and multivalent ions (even at a low concentration) can significantly worsen the stabilization and even cause it to completely fail.

Electrical double layer around a negatively charged particle
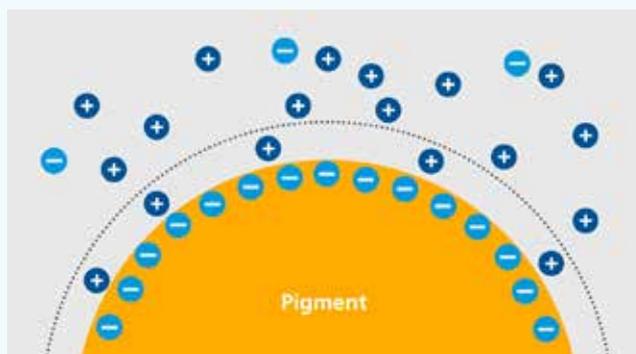
Adsorptive bound layer (Stern layer) and diffuse layer

Sodium polyacrylate as a typical polyelectrolyte
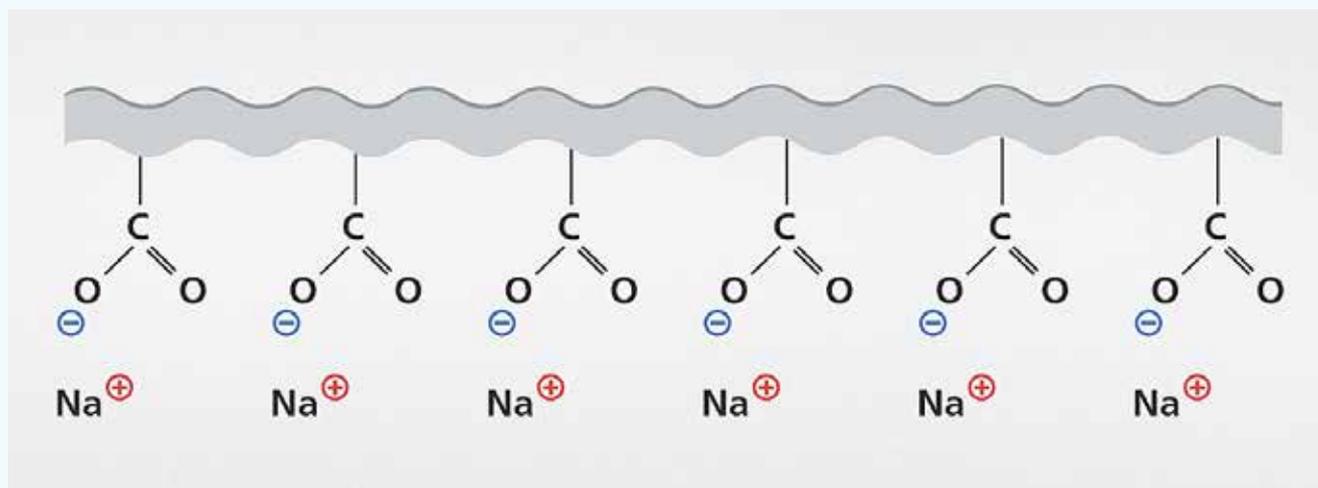
The standard dispersing additives used in the coatings industry which use electrostatic effects are polyphosphates and polyacrylates as a potassium, sodium or ammonium salt.

Alongside the influence on the charge, in some cases (dependent upon the polymer structure) a contribution towards stabilization by means of steric effects can be observed. The structure of the polyacrylates is similar to that of binders, therefore influencing the dried films less than the polyphosphates would. The phosphates have the advantage that they are also ideal for chelating multivalent ions (e.g. calcium) in the system and thereby eliminating the negative influence of these ions on the stabilization mechanism.

Dispersing additives of this type have been used successfully in aqueous emulsion paints for decades and continue to be used successfully today.

Polyelectrolyte-based dispersing additives for aqueous systems are pure dispersing additives and feature virtually no pigment wetting properties. Therefore, if the pigment wetting is also to be improved, they must be combined with the appropriate wetting additives.

07
Steric stabilization

Instead of using electrical charge, a repulsion potential can also be developed between dispersed particles by means of the adsorbed polymer coatings on the surface. Each particle is surrounded by an envelope of solvated polymer molecules and, when approaching, two particles overlap and penetrate these polymer envelopes.

This increases the polymer concentration in the overlapping area and the osmotic pressure causes the solvent to be transported to this area so that the particles are repelled away from each other again. In addition, in the overlapping area the polymer molecules are restricted in their conformation, which signifies a reduction in the entropy and therefore represents a repulsion potential. Depending on the system, an enthalpic as well as an entropic contribution can be made towards stabilization.

Gibbs/Helmholtz equation

$$\Delta G_F = \Delta H_F - T \cdot \Delta S_F$$

To prevent flocculation, the free energy, ΔGF, of this process must be positive. If both ΔHF and ΔSF are negative, yet the entropy term is greater than the enthalpy term, this results in a positive value for ΔGF and we have entropic stabilization. If ΔHF is positive, the system is truly stable and in this case we also have an enthalpic contribution towards stabilization.

Suitable additives generally have two typical structural features: firstly, 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. Secondly, such products contain **binder-compatible chains** which, after adsorption of the additive onto the pigment surface, protrude as far as possible from the pigment into the surrounding binder solution.

This layer of adsorbed additive molecules with the protruding polymer chains brings about the stabilization effect described above and therefore the deflocculation of the pigments. The effect is further intensified by the fact that the polymers of the coating binder interact with the polymer segments of the additive and can strengthen the adsorption layer.

Pigments with adsorbed additive molecules
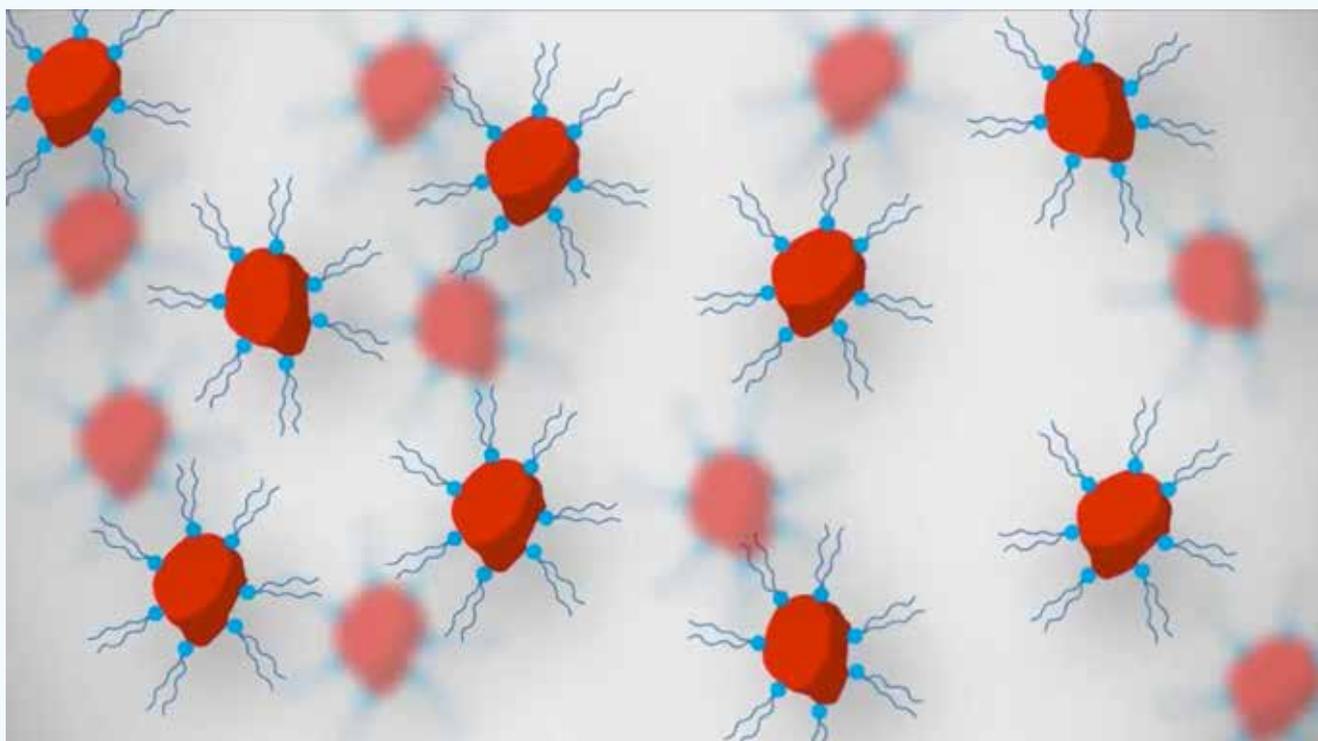
When the pigment particles approach each other, the polymer segments penetrate and this causes steric stabilization.

Through specific structural elements composed of pigment-affinic groups (polar) and binder-compatible chains (less polar), these additives exhibit definitive **surfactant properties**. In other words, they not only stabilize the pigment dispersion by means of steric hindrance, but they also function as **wetting additives**. It is therefore not necessary to add a dose of special wetting additives when using these wetting and dispersing additives.

To ensure an effective stabilization, the additive envelope around the pigment particles should be as thick as possible – a thickness in excess of around 10 nm is generally considered sufficient. This means that the polymer segments of the additive must be as highly solvated as possible, i.e. they must have a **good compatibility** with the surrounding binder solution. If there is a poor compatibility, the polymer segments will fold together and then will not lie closely on the pigment surface: the stabilization against flocculation is then marginal. When selecting an additive for a specific system it is necessary to consider the compatibility between the additive and the binder.

The mechanism of steric stabilization can be applied both to aqueous as well as non-aqueous systems; of course, the additives must have the appropriate compatibility. While the electrostatic stabilization functions virtually only in aqueous systems, this restriction does not apply to steric stabilization.

08
Deflocculating
wetting and dispersing additives

Low-molecular weight polymers

Wetting and dispersing additives have been available for a long time now, frequently fatty acid-based with an adhesive group per molecule (anionic, cationic, non-ionogenic) and which can be classified as low-molecular weight polymers. They have a deflocculating effect and have been successfully used to stabilize **inorganic pigments** and are still being used today. For example, the long-established ANTI-TERRA-U is an additive from this group that is still widely in use. Newer developments include products like DISPERBYK-107 or DISPERBYK-108 which fulfill modern requirements such as containing no aromatic solvents or no solvents at all. Products such as DISPERBYK-111 or DISPERBYK-180 are used to stabilize titanium dioxide and inorganic pigments in the automotive sector and in industrial coating systems.

However, when it is necessary to stabilize **organic pigments** (or also fine-particle carbon black pigments) against flocculation, these additives show considerable weaknesses. A durable and permanent adsorption onto the pigment surface is of utmost importance in order for additives to be effective, as this is the only way that a stable protective envelope can be formed. Inorganic pigments are ionically constructed and display relatively high surface polarities, thus making adsorption of the additives relatively easy. Organic pigments have a completely different structure. Here, the pigment crystals are made up of individual molecules which are also predominantly non-polar and held together by means of intermolecular forces. As a result, organic pigments have very non-polar surfaces and therefore make proper adsorption of conventional additives rather difficult. On account of the negligible interactive forces between the adhesive groups and the pigment surface, the dispersing additives are able to fall away from this very easily and there is no stable protective envelope around the pigment particles. In practice, this means that in many cases organic pigments are insufficiently deflocculated and stabilized using low-molecular weight wetting and dispersing additives. Moreover, this is compounded by the fact that the fine-particle organic pigments have more of a tendency to flocculate than the coarse-particle inorganic ones. As the entire pigment surface must be covered with additive molecules and, on account of their smaller particle size, the organic pigments have a greater specific surface, considerably higher additive doses are required. High additive quantities can have a negative effect on the coating film properties (e.g. hardness, water-resistance).

Low-molecular weight wetting and dispersing additives
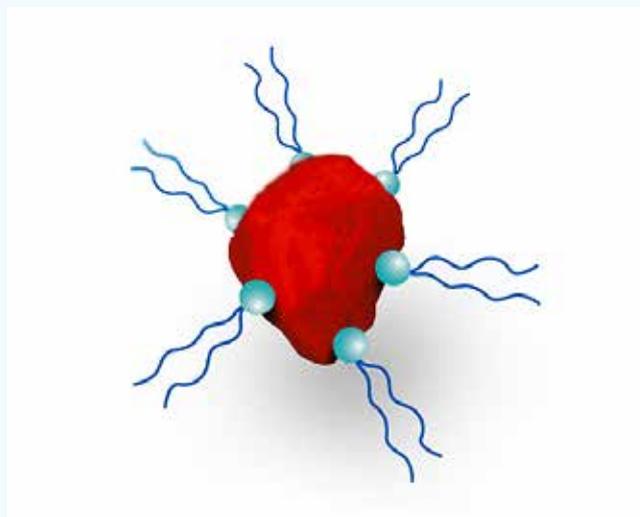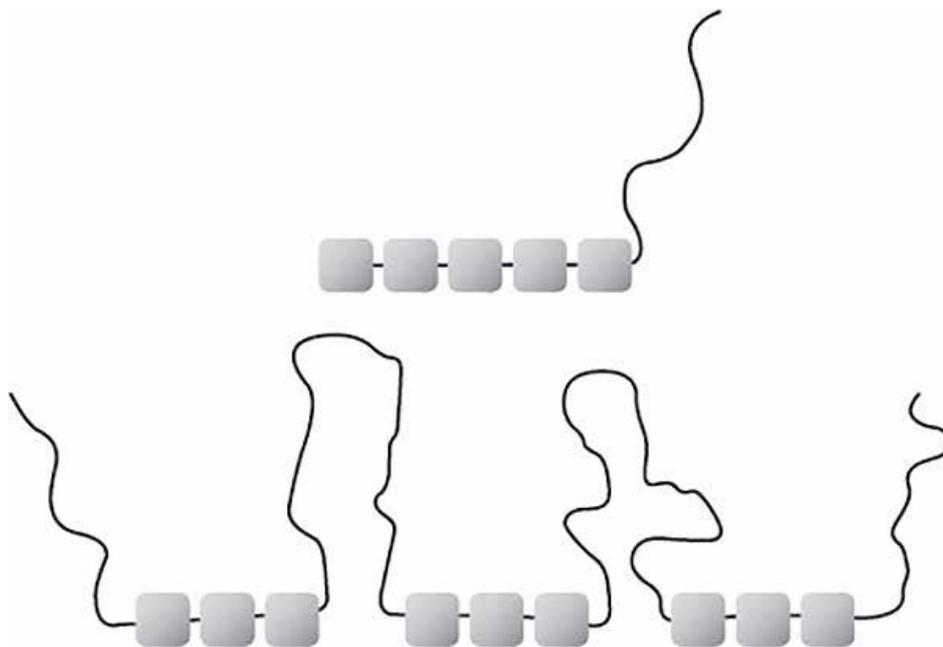
High-molecular weight polymers
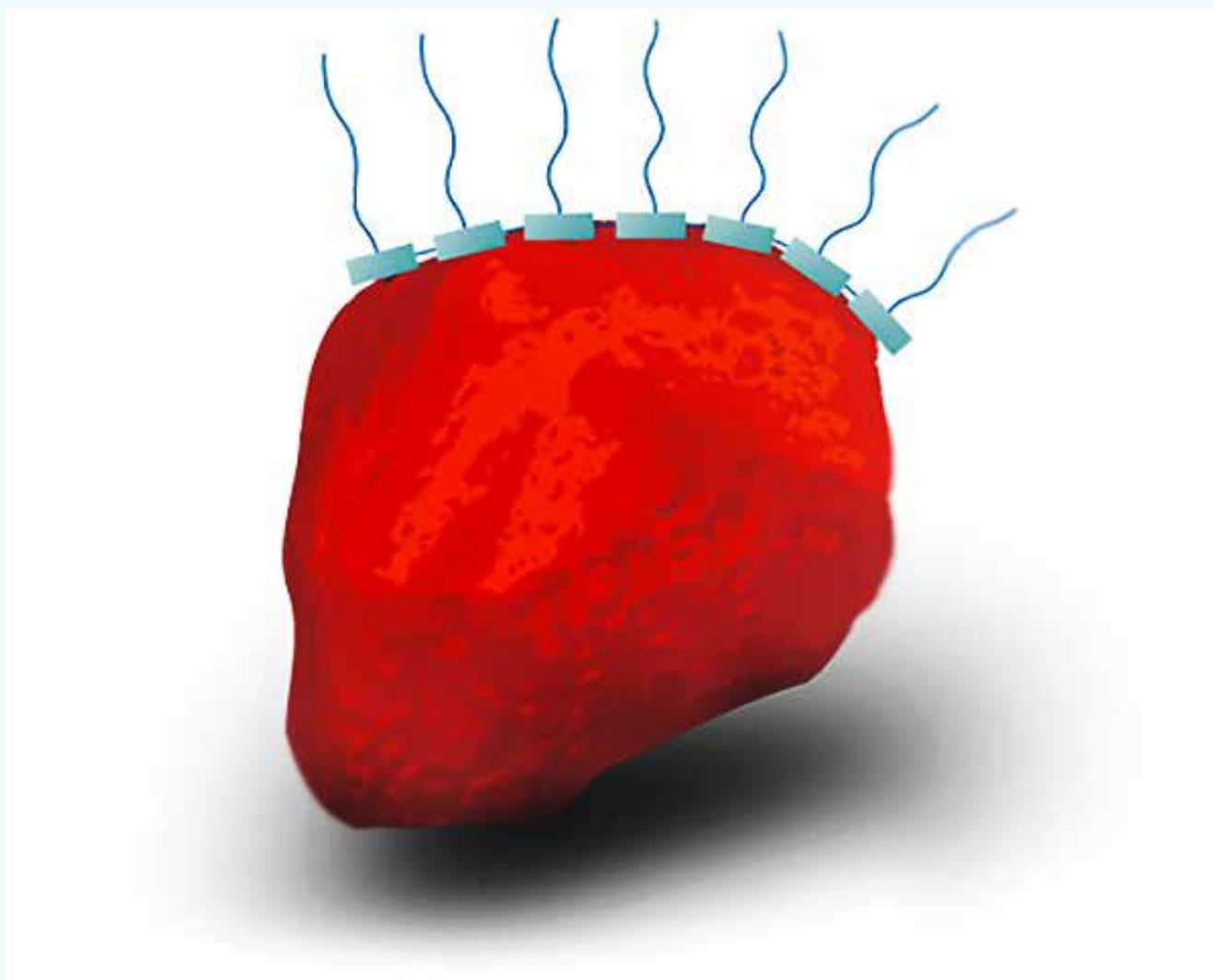
Polymer wetting and dispersing additives: a multitude of anchor groups ensure good adsorption even on less polar pigment surfaces, e.g. in the case of organic pigments. The highly solvated polymer segments, which are also protruding from the pigment surface, cause a steric stabilization of the pigments.

For the most varied of reasons, in the past increasingly more organic pigments have been used (e.g. for heavy metal-free, more brilliant shades) and this trend has led to the development of a new group of additives: polymeric wetting and dispersing additives. They differentiate themselves from conventional low-molecular weight products primarily by two structural features: on the one hand, they have a considerably greater molecular mass and thereby a character similar to that of a binder. However, that is just a side effect; what is more significant is that these additives contain a very large number of adhesive groups. The molecule has to be enlarged in order to accommodate all these adhesive groups. Even if the adsorption of an adhesive group on the pigment surface is only weak, the large number of contact points between the additive and the pigment achieves a stable, durable adsorption even on organic pigments. These additives develop their stabilizing effect – the same way as conventional products – by steric hindrance as a result of the polymer segments which are protruding into the binder solution.

Optimal stabilization is possible only when such polymer chains are properly unfurled and therefore quite compatible with the surrounding polymer solution. If this compatibility is restricted, the polymer chains collapse. Consequently, all chances for steric hindrance and the resultant stabilization are lost. The compatibility of highly polymeric additives with various coating binders 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.

Segments with adhesive groups and binder-compatible segments in the form of polymer loops and chains can be combined with each other in a variety of ways. Statistical blocking and plugging copolymers have already proven successful. A number of factors are important for a good steric stabilization of the deflocculated pigments. The molecular mass and the molecular mass distribution play a key role alongside the polymer architecture.

Different combinations of segments with adhesive groups and binder-compatible side chains are possible with polymeric wetting and dispersing additives.

The high-molecular weight wetting and dispersing additives have indeed been specially developed for organic pigments, but are actually just as suitable for inorganic pigments and particularly also for stabilizing **pigment blends**.

Major additives in this group are DISPERBYK-161 for high-quality industrial coatings such as automotive coatings and DISPERBYK-2163 or DISPERBYK-2164 (no aromatic substances) for a wide range of industrial applications. These additives contain cationic anchor groups which, in isolated cases, may interact with acidic components in the coating formulation (e.g. acid catalysts in coil coatings). In such cases, additives from our DISPERBYK-170 or DISPERBYK-174 families are recommended. They make use of a different adhesive group chemistry and thus avoid such problems. In addition, there are modern branched structures with sterically hindered cationic adhesive groups (DISPERBYK-2155) or complex core shell polymers where the pigment-affinic block is encapsulated (DISPERBYK-2152). This reduces the reactivity of the additives in view of the coating systems to a minimum with the constant effectiveness in the stabilization of inorganic and organic pigments as well as carbon blacks.

Aqueous coating systems

In aqueous systems which are based on emulsion binders and primarily for emulsion paints and plasters which are used in the area of architectural coatings, the pigments are predominantly stabilized by electrostatic repulsion. Ammonium salts of polycarboxylic acids (such as BYK-154) are frequently used.

In principle, aqueous systems that are based on water-soluble binder solutions or combinations of such binder solutions with binder solution emulsions (hybrid systems) can also use electrostatic repulsion for pigment stabilization. However, in practice it is found that steric stabilization with polymeric wetting and dispersing additives is frequently preferred, especially in high-quality industrial coatings. The mechanism works the same way as in solvent-borne coatings, the only requirement being that the polymeric additives must be polar enough to ensure compatibility with the aqueous surroundings. It is not necessarily desirable for such additives to be water-soluble since too high a polarity could adversely affect the durability of the coating film (e.g. water-resistance). Typical products representing this additive group are DISPERBYK-184, DIS-PERBYK-190, DISPERBYK-194 N and DISPERBYK-198.
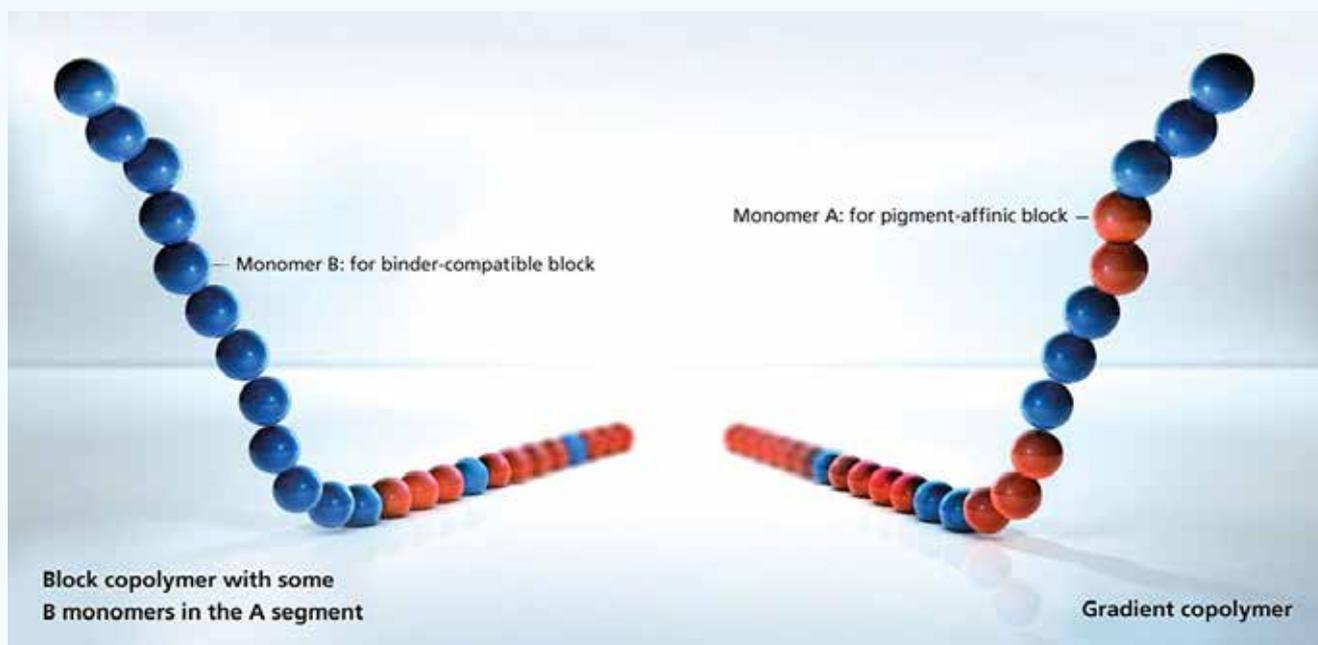
09
Modern polymerization methods

To synthesize effective additives, not only must the appropriate number of monomers for the pigment-affinic groups and the binder-compatible chains be selected, but their arrangement in the copolymer is also crucial. If the individual components are statistically distributed along the chain, the additive effect that is desired will not be observed. **Block structures** are more favorable for wetting and dispersing additives. These comparatively simple structures can be modified to include a lot more intricacies and details:

the segments consisting of A monomers (pigment-affinic groups) do not need to be compatible with the binder system, because the B segments are responsible for this compatibility. However, if their incompatibility is too great, the handling of the products becomes difficult and the efficiency is reduced. Therefore it can be beneficial to have some B monomers within the A segments in order to improve the compatibility. Another possibility is to reduce the sharp transition between an A and a B block by creating smoother transitions: the concentration of A monomers reduces along the polymer chain while the B monomers increase (gradient copolymers).

Examples for modifying the fine structure of block copolymers when using controlled polymerization technology (CPT)

Monomer A: for pigment-affinic block —

— Monomer B: for binder-compatible block

Block copolymer with some
B monomers in the A segment

Gradient copolymer

The knowledge about interactions between the structure of copolymers and their efficiency is only helpful when it is possible to reproduce the complex copolymer structures not only in the laboratory but also under production conditions. And in this respect, the situation today looks much better than it did in the past. For some years now, modern polymerization methods (ATRP, NMP, C-RAFT, S-RAFT, GTP) have been available to provide a very high control of the structure of copolymers. These methods (the first four are often summarized as "CRP", controlled radical polymerization) all have their specific features and advantages/disadvantages and can be used to polymerize a wide range of monomers under controlled conditions. DISPERBYK-2000 and DISPERBYK-2001 were our first wetting and dispersing additives produced by controlled polymerization (GTP) and were introduced in 1999. Newer products such as DISPERBYK-2010, DISPERBYK-2012 and DISPERBYK-2015, all of which were developed for modern aqueous systems, make full use of the possibilities that modern CRP methods offer today. And it isn't just the sequence succession in the block copolymers that can be better controlled and reproduced, but also the molecular weight distribution has become considerably tighter which, for example, makes it easier to handle the additives.

10
Controlled flocculation

The term "flocculation" carries rather negative connotations; however, there are certain conditions under which controlled flocculation may actually be more desirable than complete deflocculation. An uncontrolled flocculation will in any case make the color location unstable during storage, will cause too much precipitate, reduce gloss and increase the viscosity. Controlled flocculation has been used in the coatings industry for many years.

Flocculation
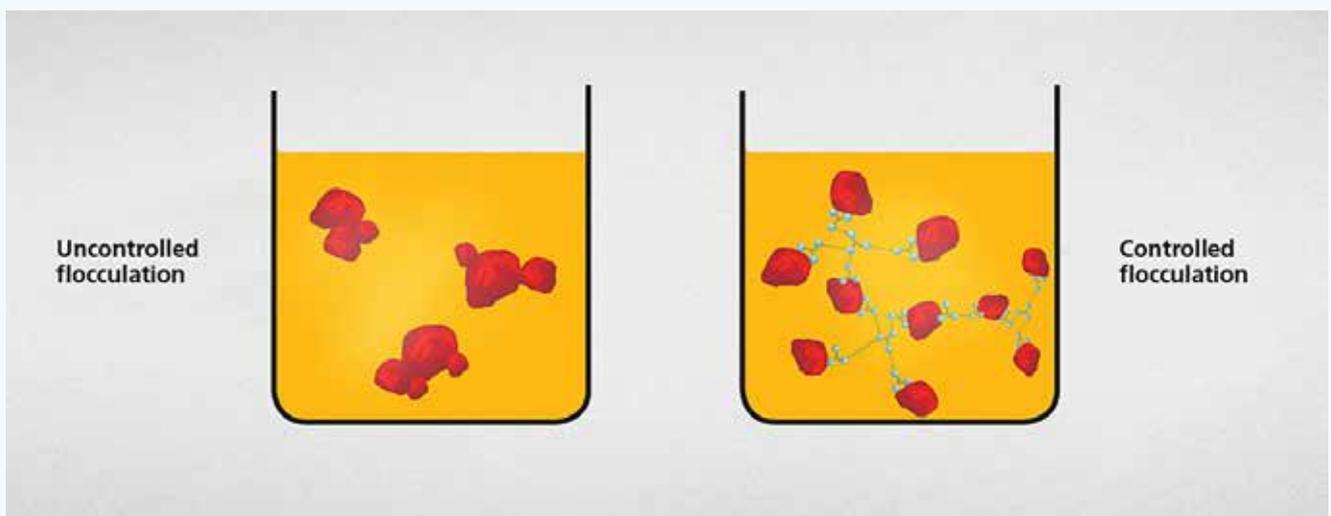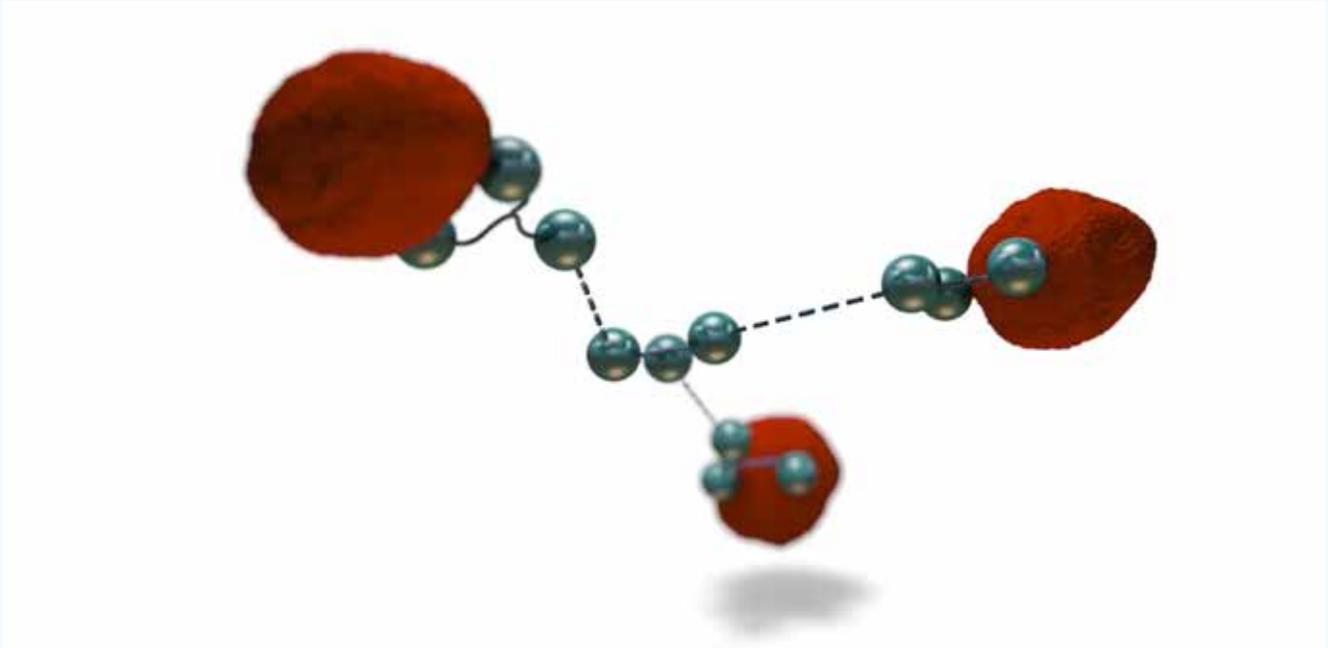

Uncontrolled flocculation (without additives): flocculated pigment particles have direct contact with each other and can be separated only by considerable shear forces.
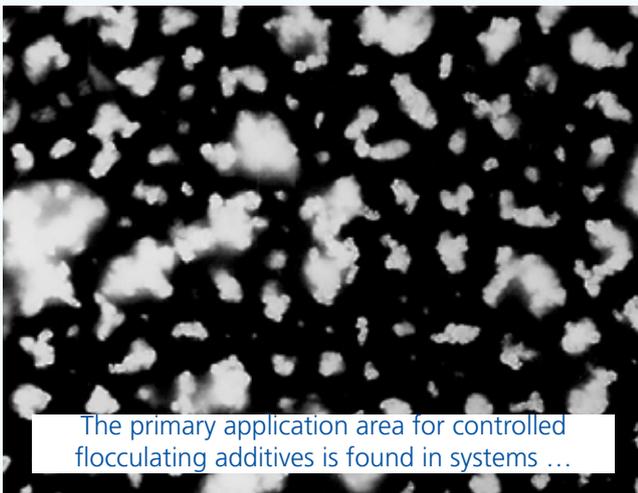
Controlled flocculation (caused by additives): additive molecules cause the pigment particles to form a network; no direct pigment-pigment contact. Such "controlled" flocculates can be destroyed by low shear forces.

If low-molecular weight wetting and dispersing additives contain at least two to three adhesive groups which are kept apart from each other, then they can form **bridges** between different pigments either directly or via further additive molecules, and in this manner they can develop larger three-dimensional **network structures** that are similar to flocculates.

The size and stability of such "flocculates" are determined by the properties of the additive – in particular, through the additive-additive and additive-pigment interactions. We consider this to be a "controlled flocculation", as the entire process is controlled by the additive.

Controlled flocculate with special low-molecular weight wetting and dispersing additives with several adhesive groups per molecule.

The primary application area for controlled flocculating additives is found in systems …
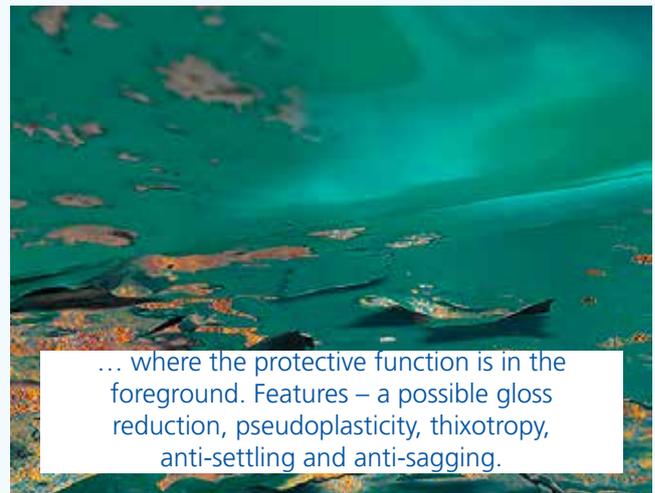
… where the protective function is in the foreground. Features – a possible gloss reduction, pseudoplasticity, thixotropy, anti-settling and anti-sagging.

While deflocculation is used …

… when an optimal appearance is required. Features – high gloss, lower viscosity and good leveling.

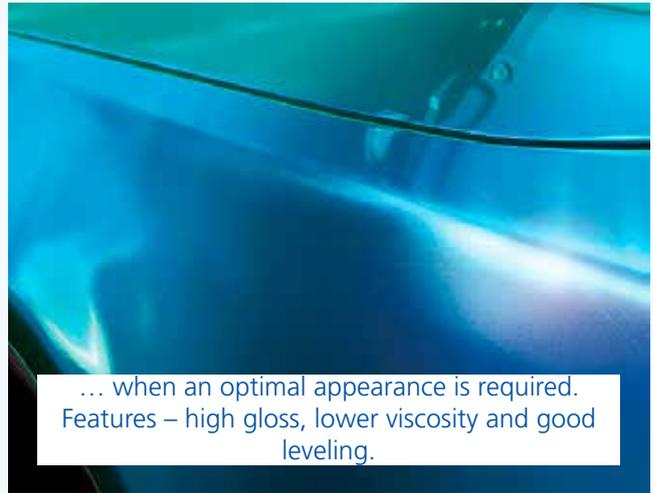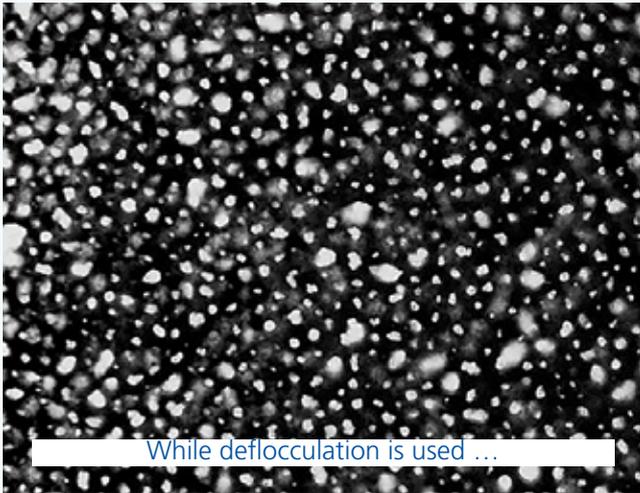It is important to clarify the difference between the above flocculation state and the "normal" flocculation state: without additives, the pigment particles in the uncontrolled flocculate are in direct contact with each other and it is difficult to separate them. A controlled flocculation, however, ensures no direct pigment-pigment contact as additive molecules are always located between the pigment particles. These wetting and dispersing additives which have a controlled flocculating effect also have pigment-wetting properties and they also stabilize the pigment dispersion, only in a different manner to that of the deflocculating additives.

Although uncontrolled flocculation is always undesirable (since a variety of negative effects occur, like, for example, gloss reduction, viscosity instabilities, etc.), controlled flocculation can purposefully be used to attain certain desired effects in the coating system.

The three-dimensional network structure created by controlled flocculating wetting and dispersing additives has a similar form to that of rheology additives and a characteristic rheological behavior is linked to the controlled flocculating additives: through these structures, the resting state viscosity of the coating is really high. However, when shear forces are applied, the structures (pigment flocculates) break apart and induce lower viscosity. Afterwards, following the removal of the shear forces, the flocculates are able to rebuild. Generally, such systems display a flow threshold. While the deflocculating additives present rather Newtonian flow characteristics and break down thixotropy, when a controlled flocculating additive is used, thixotropy or at least pseudoplastic flow characteristics are generated. Through the above rheological behavior, properties such as sagging and settling can be positively influenced. That said, controlled flocculation also brings with it a gloss reduction; it is not possible to create high-gloss formulations with these additives.

Taking into consideration these discussions, it is also clear where dispersing additives of this nature can be used: they are mainly used in primer surfacers, fillers and intermediate coats where it is not essential to achieve a high gloss, but an improved stability on suitable surfaces and a decreased tendency of the solid particles to settle are desired. However, for topcoat systems where a better gloss and leveling are required, it is usually preferred to have extensive deflocculation. Of course, we do have a middle ground here. If it is not necessary for the topcoat to be of a very high quality, you can also achieve good results by using a slightly controlled flocculation.

However, the distinctive rheological effects of the controlled flocculating additives should not obscure the fact that these products are primarily used for wetting and stabilizing pigments. The influence on the rheology is only a side effect, even if it is very convenient. It is often the case that it is insufficient to influence the flow characteristics using the controlled flocculating dispersing additives alone. It is common practice to combine these with "true" rheological additives.

The most widely used controlled flocculating wetting and dispersing additives are ANTI-TERRA-204, which is used in a variety of ways in solvent-borne fillers and primer surfacers, and ANTI-TERRA-250, which is applied in aqueous systems. BYK-P 104 is an additive which has a much less controlling flocculating effect. It was developed to combat separation in combinations of titanium dioxide with colored pigments. It achieves this by means of co-flocculation, without having any adverse effects upon gloss and rheology.

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Prevention of floating

Commercial coating formulations are rarely monopigmented; they are usually **blends** of two or more different pigments. Of course, all the pigments in these systems should also be wetted well and extensively deflocculated. However, this can cause another issue: ideally, all pigments are evenly distributed throughout the entire coating film; however, if this blend is disturbed, the pigments separate from each other, and this can cause color changes in the coating. This defect is known as **"floating"**.

One of the causes for the pigments to become separated from each other is flow effects in the dry coating film. Solvent must be transported from the lower coating layer to the surface. Evaporation causes the density of the remaining materials to increase and the solvent then sinks again.

In addition, evaporation causes cooling effects and the surface tension changes. All of this leads to the development of eddy currents which arrange themselves in the form of more or less equal hexagonal cells (so-called **Bénard cells**). In the center of the cells, the coating material rises and then distributes itself across the surface and then flows back down along the cell borders. These cell flows have been known for a long time – not just in coatings – and occur in every liquid coating film (even non-pigmented ones). In a pigmented system, the pigments also participate in these eddy currents and provided the **mobility** of the different pigments is similar, they are also transported into the eddy currents in a very similar manner and cannot be separated. If, however, the pigment mobility is considerably different, then the transport behavior is also different and can lead to separation.

Differences in the pigment mobility are often the main reason for pigments to no longer be homogeneously distributed. When solvents evaporate from a dry coating film, eddy currents (Bénard cells) form. Such movements cause small differences in temperature, density, and surface tension. The pigments participate in such movements, and the different pigment mobilities can cause the pigment to separate. This differential mobility can be equilibrated through the usage of controlled flocculating additives.
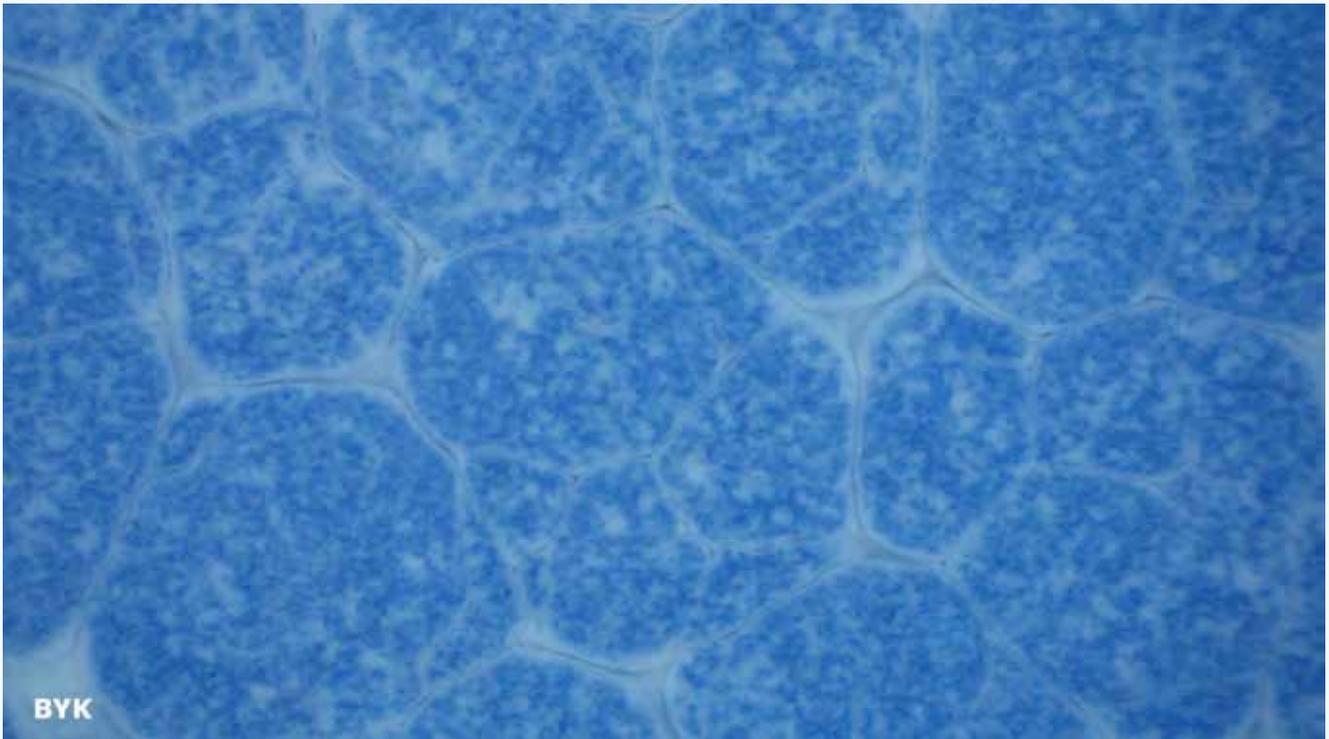
Eddy currents in a liquid coating film (Bénard cells). Example of a coating pigmented with phthalocyanine blue and titanium dioxide, where it is easy to see how the titanium dioxide has accumulated along the cell borders and gives the surface an irregular, blotched appearance.

Horizontal separation ("floating")

Even color on the surface

Color shift in the lower layers
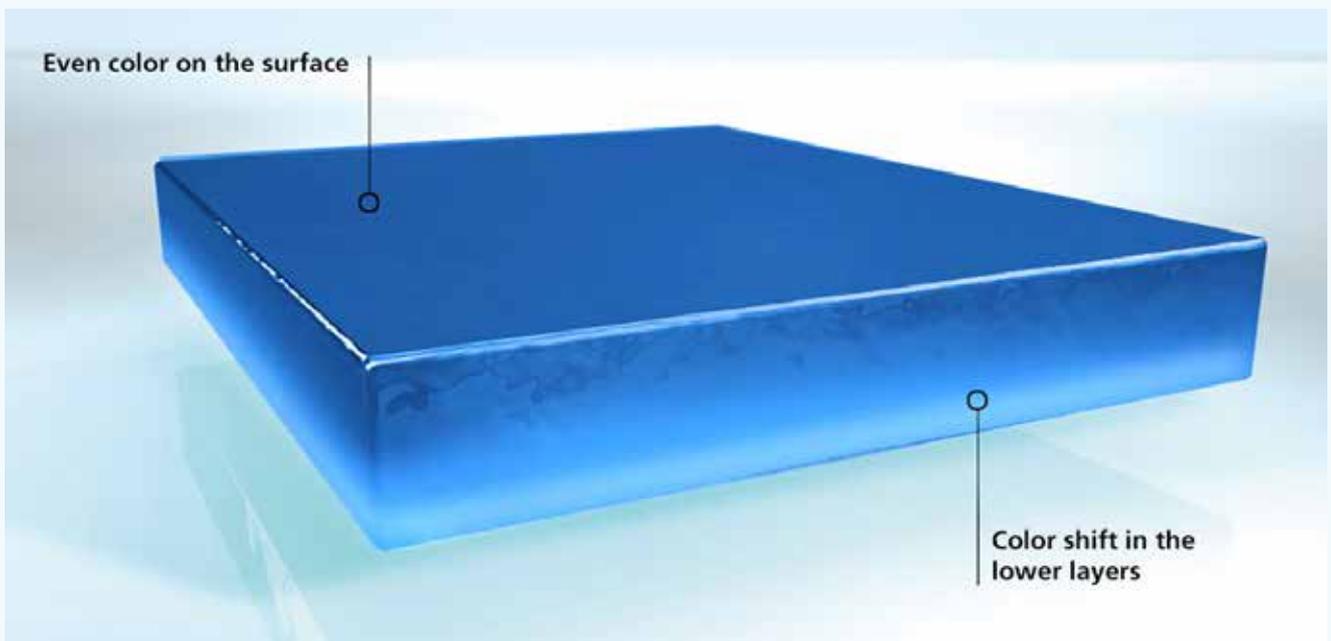
A pigment type has then concentrated itself on the surface and, in this case, the coating film has a uniform color on the surface (which, however, is not the original color of the pigment blend). The defect is only visible when the **rub-out test** is carried out. This test involves rubbing a small area of the still wet coating film with a finger, i.e. a homogenous blend of the different pigments is created in this area. The instability of the pigment blend is shown by the fact that a color difference is evident between the rubbed area and the surrounding coating material. This color difference can also be measured (as ΔE) and used as a quality criterion.

To avoid floating defects, we have to influence the mobility of the pigments. We have to make the mobilities of the various pigment types as similar as possible. One option is to use controlled flocculation. Controlled flocculating additives incorporate the different pigments together in the flocculate and therefore forcibly adjust their mobility. The targeted co-flocculation of the different pigment types therefore combats separation.

Of course, on account of the possible gloss reduction and more unfavorable pigment utilization, flocculation – even a controlled one – is not particularly desired in many topcoat systems, especially high-quality ones.

Polymeric wetting and dispersing additives can provide a solution here. They have proven performance in equilibrating pigment mobility, while simultaneously providing complete deflocculation of all pigments. Through the interaction of the adsorbed polymeric additives with the surrounding binder solution, the deflocculated pigment particles are tightly incorporated into the binder system and their mobility reduced.

This explains how floating can be eliminated even in the presence of smaller, deflocculated organic pigment particles and larger, inorganic pigments, as all the pigments have similar mobility.

Rub-up test

Without wetting and dispersing additive

With wetting and dispersing additive

Strong color difference

Minimal color difference

BYK
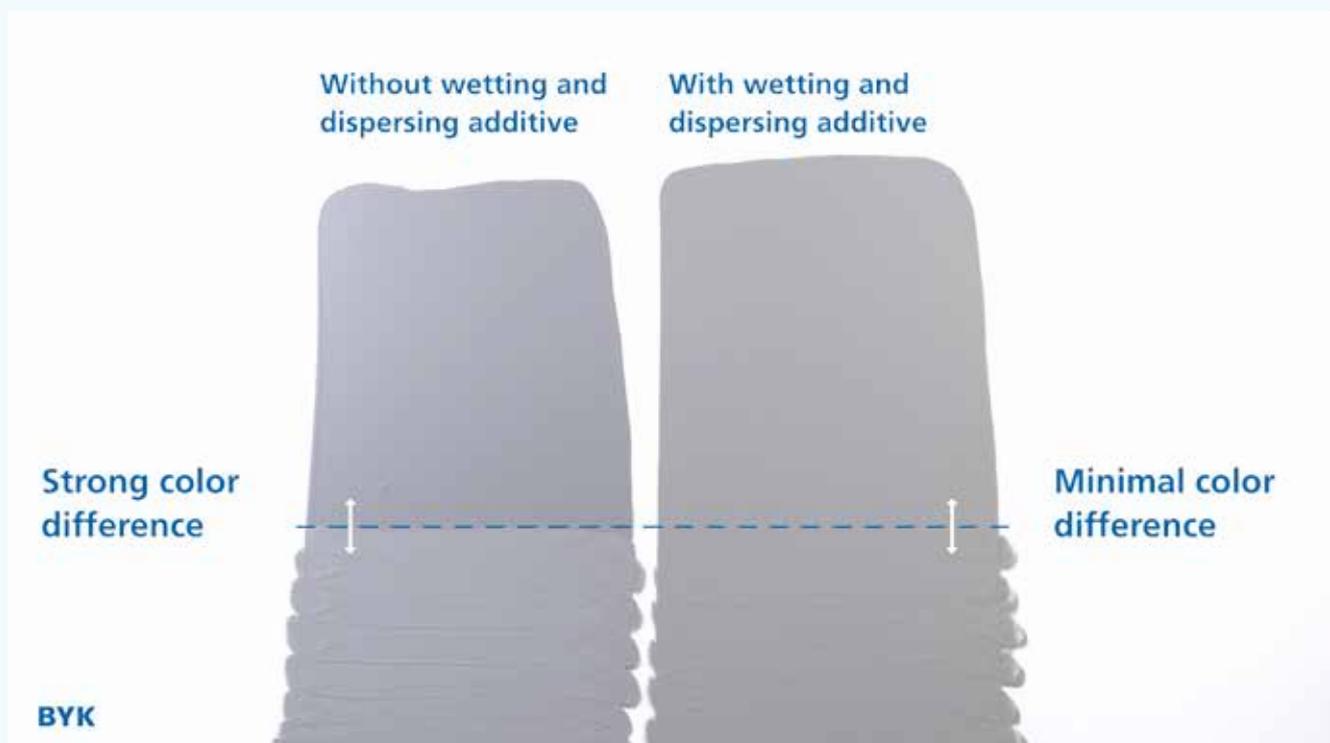
Preventing separation in pigment blends using wetting and dispersing additives (the rubbed area is at the bottom in each case)

| Without additive | With additive | With additive | Without additive |

Phthalocyanine blue + TiO$_2$ Red iron oxide + TiO$_2$
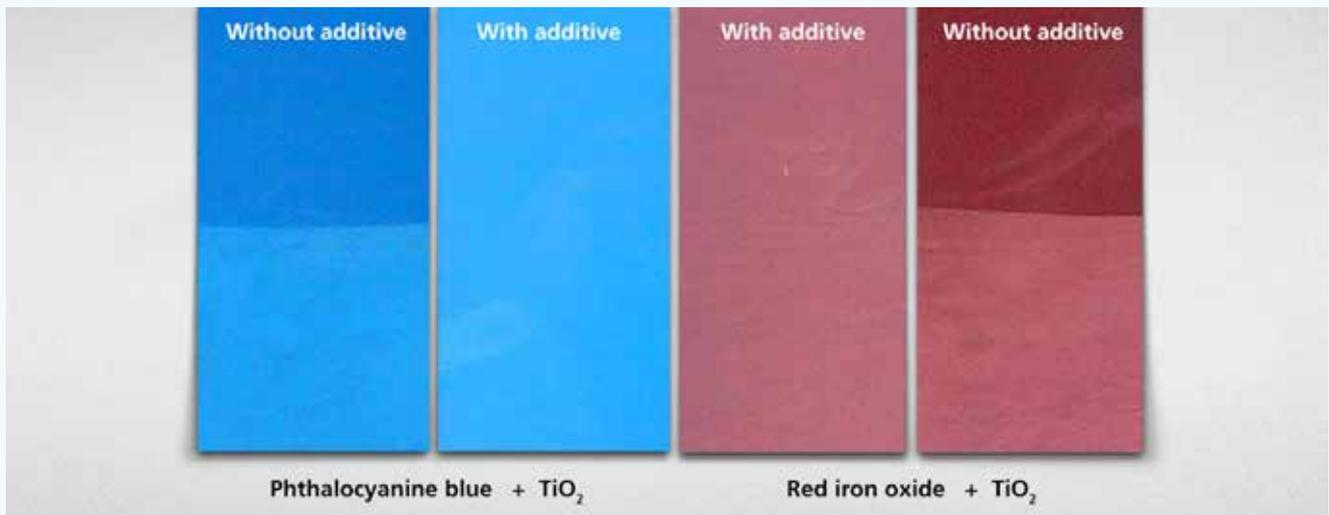
In non-aqueous systems, electrical charges on the pigment surface are usually so weak that they play no major part in stabilizing the pigments against flocculation. Unlike charges of the pigments can, however, have negative effects on the stability of pigment blends and therefore the floating behavior. The charge carried by a pigment depends not only upon the pigment itself, but also upon the binder solution: a pigment that is ground in different binders can display different charges. Different pigments that are ground in the same binder can also display different charges. Obviously, strong flocculation can occur when different pigment charges exist within the same coating.

It is important to note in practice that the pigment charge can also be influenced by the dispersing additive that is used: some polymeric additives are capable of equilibrating differently charged pigment particles in their electrical charge. The additive provides an additional stabilizing effect: the polymeric additive equilibrates not only the mobility of the various pigments (in addition to providing steric stabilization), but also ensures that all the pigment particles carry the same charge, thereby avoiding any instability due to charge differences.

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Pigment concentrates

Pigment concentrates (pigment pastes) are monopigmented systems with as high as possible pigment content and as little as possible binder (grinding resin). They are used in two ways in the production of coatings.

For tinting: After the grinding and finalization, the pastes are used for the final fine adjustment of the color, i.e. for nuancing. In this case, only a small percentage of the pastes are used. The individual components of the pigment concentrates (especially the grinding resin) then have virtually no obvious influence on the quality of the coating that has been tinted.

For production: A coating can also be made up entirely of a blend of pastes and then let down with the desired binder (as a clear coating or white coating). Greater quantities of pigment pastes are required for this. As the pastes then have a significantly greater influence on the coating quality, the requirements on the quality of the pigment concentrates are also considerably greater.

While it has always been conventional practice to use tinting pastes, it is only in the recent past that the option of making coatings made entirely from paste blends has been more broadly received. Pastes are then used for production if the coating application is comparatively small, but a broad spectrum of colors and binder systems needs to be covered (typically, for example, with industrial coatings).

Manufacturing from pastes is quicker than manufacturing using a millbase and the coating manufacturer can respond more flexibly to customer requirements. Pigment concentrates can also then be used in automated coating production, as this is only possible if pumpable pastes are used instead of powdered pigments.

There are generally two possible variants. You can design a series of pigment pastes which are to be used only for one unique coating system. The actual coating binder is then also used as the grinding resin for the pastes. Such pastes can be optimally used in the coating system.

The other option is to develop a "universal" series of pastes which is compatible with most binders and can therefore be used to produce very different coating qualities. Of course, **"universal pastes"** will not necessarily be ideal for each type of coating binder. Compromises are inevitable in such cases.

Requirements for pigment concentrates

The **stability** of the paste is one of the key requirements. No flocculation, no settling and no syneresis may occur during the, at times, very long storage periods. The paste should contain as much pigment as possible and contain as small as possible amounts of the other components. Nevertheless, the paste must be easy to handle, i.e. capable of flowing or being pumped, and it must not have a tendency to dry out.

It must be possible to easily incorporate the paste in all types of binder. On one hand, this is a question of compatibility; on the other hand, you have to exclude any shock phenomena (dispersion of the pigments).

Finally, the coating film properties, in particular the resistances, must not be negatively influenced by the paste content.

To comply with the specified requirements, it is absolutely necessary to use additives in the pastes. It is only by adding a suitable **wetting and dispersing additive** that the paste viscosity will reduce sufficiently for the pigment content to increase. Simultaneously, the pigment is deflocculated; a prerequisite for high-gloss and color-stable topcoats. Stabilizing the pigment dispersion by using additives also prevents shock phenomena when mixing the pastes and when finalizing.

In order to suppress floating as much as possible, alongside the deflocculation it should also be ensured that the pigment mobilities are adjusted and like pigment charges are provided.

Composition of pigment concentrates

The key component of a pigment concentrate is the **pigment**; the pigment content should be as high as possible. In addition, a **grinding resin** is required in most cases in order to obtain a storable paste and to ensure that the paste can be easily incorporated in the finalizing binder without any shock phenomena. The grinding paste is primarily chosen based on its compatibility. Its percentage of the paste should be a low as possible. If special dispersing additives are used, **binder-free** pigment concentrates of impeccable quality can also be formulated.

In addition to the solvent which is added via the grinding resin, it is usually necessary to add an additional **solvent** in order to produce a manageable paste. Choosing the correct solvent can also have an influence on the storage stability of the paste.

A suitable deflocculating wetting and dispersing additive is indispensable for a high-quality pigment concentrate. Since both inorganic and organic pigments need to be stabilized, **polymeric additives** are particularly ideal as paste additives. It must be ensured that the additive is compatible with the binder that is being used in the paste.

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Practical hints and suggestions

To achieve an optimum result using wetting and dispersing additives, a few hints and suggestions should be observed when using these products.

Incorporating the additives

Additives are frequently added to the coating during the finalization phase. However, this procedure is not suitable for wetting and dispersing additives. As these additives are needed to accelerate pigment wetting and pigment dispersion, they must be **added to the millbase** and ground with it. Only in this way can they be fully effective. If, in exceptional circumstances (e.g. for batch correction purposes), it is necessary to add the additives later on, they must be incorporated using as high as possible shear forces; it is preferable to run the system through the dispersing unit again. Nevertheless, you will find in the majority of cases that wetting and dispersing agents which have been added in this way are less effective and require greater doses.

Dosage

How much additive do you need to add? The correct dosage is key to the effect. Since the additive is designed to attach to the pigment surface, the required dosage of additive depends upon the amount of pigment surface present. Apart from a few exceptions, calculation formulas which link the additive dosage with, for example, the BET surface of the pigments or the oil number, are not particularly reliable and should be used only for specific pigment types. In practice, you would tend to base the dosage on the recommendations of the additive supplier and then develop a **series of laboratory tests** in order to optimize the dosage for your needs. You can use, for example, gloss and haze values of the coatings and the ΔE of the rub-up test as test criteria.

In the case of classic wetting and dispersing additives based on low-molecular weight polymers, a dosage of 0.5-2% for inorganic pigments and 1-5% for organic pigments are standard (additive delivery form based upon pigment weight). Typical additive dosages for polymeric wetting and dispersing additives are 1-10% (inorganic pigments) and 10-30% (organic pigments). In the case of very fine-particle pigments (e.g. some carbon blacks), greater dosages of up to 80 or 100% are required for very high-quality formulations. As these pigments can be found only in small quantities in the formulation, the additive dosage refers to the entire formulation, but is still not excessively high. A greater dosage will not have any negative effects on the coating film properties as the polymeric additives have a character that is similar to that of binder.

We should emphasize once again that all pigments must be stabilized in a coating formulation. Stabilization is also essential for allegedly "simple" pigments, such as titanium dioxide; otherwise, when mixed with other (well-stabilized) pigments there will be inevitable floating issues.

Single grinds/co-grinds

Whenever just one pigment is being dispersed, all the parameters (additive dosage and grinding conditions) can be optimized. The end result is the best possible grind quality. However, in practice, a co-grinding of all pigments is preferred to the more time-consuming single grinding process. Compromises in regard to grinding parameters are therefore necessary and the result cannot always be compared with the single grinding process. At least when working out a new formulation in the laboratory, you should always take into consideration the individual ground pigments. This way you can identify any "difficult" pigments. The subsequent procedure should be determined on an individual basis, e.g. problematic pigments can be exchanged for other pigments, they can be ground separately, or can even be added as pigment concentrates.

Pigment surface treatment

Virtually all of today's standard pigments have been provided with surface **post-treatments** of varied chemical nature. The pigment manufacturer applies these during the production of the pigments. The purpose of the surface treatment is to facilitate and improve the wettability, dispersion and stabilization of the pigments. In the case of wetting and dispersing additives, this means that they do not come into contact with the actual pigment, they are in contact with the chemical surface treatment on the pigment. Therefore, in practice, if there are unsatisfactory grinding results with a specific pigment, the same pigment should also be considered with other surface treatments.