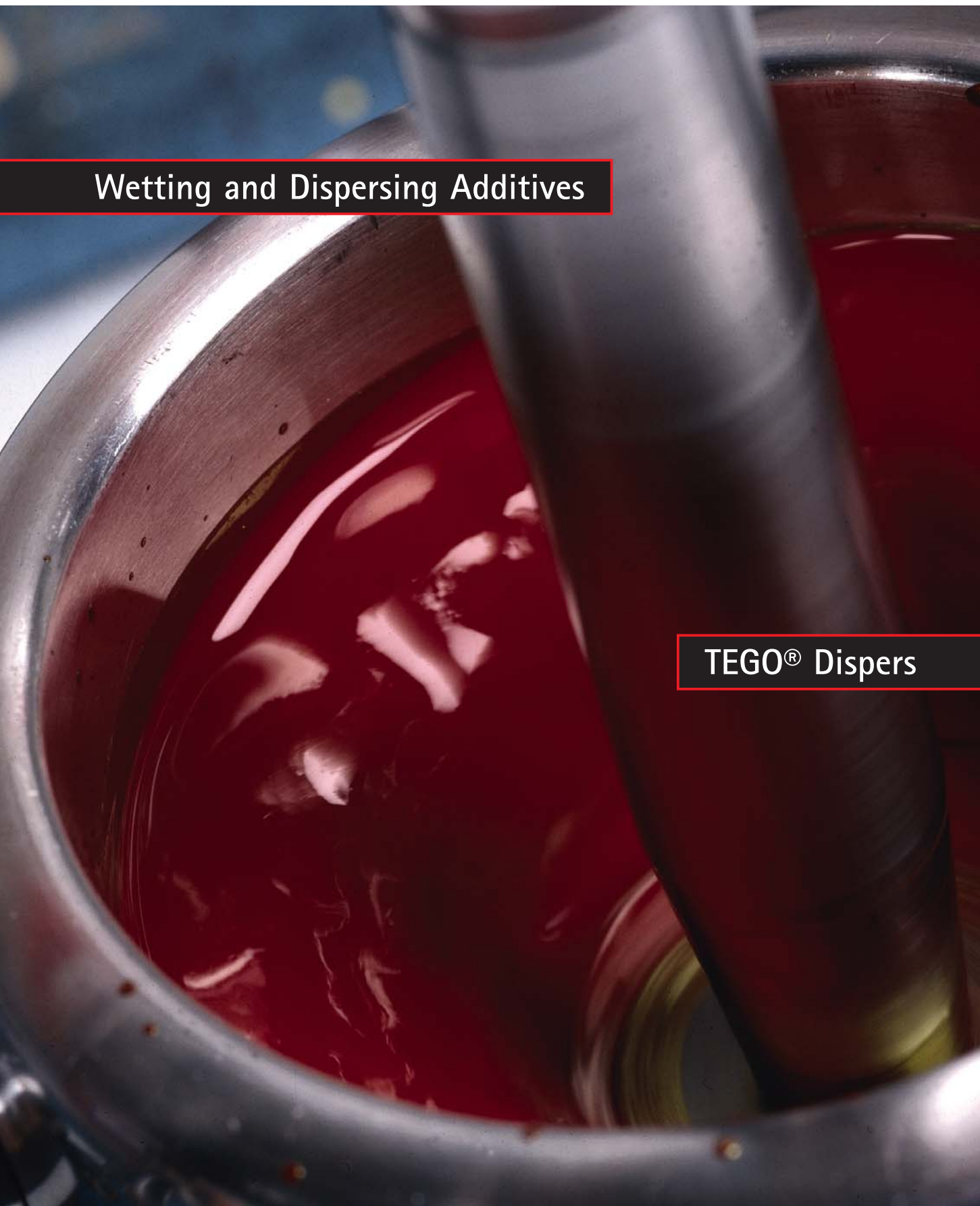


## Wetting and Dispersing Additives

TEGO® Dispers



Anyone who has ever stirred up sand and water in a bucket knows how difficult it is to form a stable, homogeneous mixture from an insoluble solid and a liquid. A similar process must be mastered in the manufacture of pigmented paints and coatings. Only pigments with

very small particle sizes between 0.05 and 0.5  $\mu\text{m}$  can impart optimum color and protection. It is therefore necessary to reduce the size of the pigments as commercially supplied. In the dispersion process the insoluble pigment is broken down, finely dispersed and stabilized in

the liquid paint formulation. It is almost impossible to do this without using wetting and dispersing additives. These additives are extremely important for the coatings industry because of their very wide range of functions.

## The function of wetting and dispersing additives

While wetting and dispersing additives lower the viscosity of a paint formulation, that is certainly not their only effect. This class of additives has a major influence on a wide range of essential characteristics of the formulation:

**Color strength:** Color strength is a measure of the ability of a pigment to absorb incident light and color a medium. It has practical importance in coloring white base paints: the stronger the tinting agent the more cost-effective it is. The color strength of such a preparation depends mainly on the intrinsic absorbance and average particle size of the pigment. The smaller the pigment particles, the greater is their effective surface area and therefore the higher their absorbing power. Higher absorbing power goes hand-in-hand with higher color strength. Smaller pigment particles must be stabilized using dispersing additives, so that they remain finely distributed and do not clump together into aggregates.

**Hiding power:** The hiding power of a coating is its ability to cover a color or the color difference with the substrate. How well the substrate is covered depends on the thickness of the coating, the color of the substrate and also on

the scattering power of the pigment and the refractive indices of the pigment and binders. In a coating with strong hiding power, the pigment particles scatter the incident light so strongly that hardly any of it reaches the substrate. Any remaining light reflected from the substrate is then so strongly scattered that it no longer reaches the eye. For a coating to scatter light optimally, an even, fine distribution of pigments stabilized by dispersing additives is essential.

**Flocculation:** Flocculation is the re-agglomeration of previously dispersed particles. In the dispersion process, pigments are broken up by inputting energy and forming new surfaces. However this is an unstable state. Flocculation can occur at any time during paint manufacture, storage or application. Pigments also tend to flocculate after the paint has been applied to a surface. Carbon blacks, with large surface areas, show this tendency and, if this happens, a substrate cannot be evenly covered in black. Dispersing additives inhibit flocculation of the pigment particles.

**Gloss:** Light reflected from a surface contains specular and diffuse components. High gloss occurs when the sur-

face is very smooth and the diffuse component of the reflection is very small. Pigment particles or flocculates which protrude from the surface disturb the specular reflection. Flocculated pigments can also affect leveling. Poor leveling reduces the gloss even further. In as far as wetting and dispersing additives inhibit flocculation, they improve the gloss of a coating.

**Flooding and floating:** These phenomena occur with mixed pigments when the densities and/or particle sizes of the pigments differ strongly. With its high density, titanium dioxide tends to concentrate at the bottom of the drying paint film. Organic colored pigments have a noticeably lower density than titanium dioxide and therefore concen-

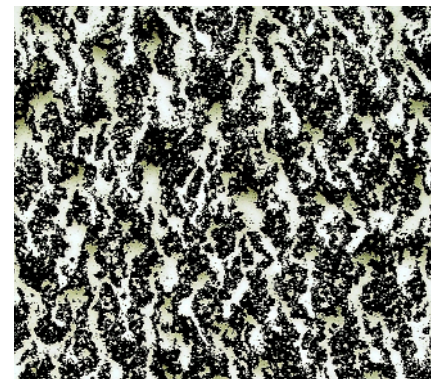


Figure 1: Flocculation of carbon black in a solvent-borne coatings system

trate in the upper part of the film. This vertical flooding, also called floating, causes the paint film to appear more colored than intended. Flooding can be demonstrated by rub-out tests (see page 86).

Horizontal flooding occurs by separation of the colored pigments in the drying paint and stems from solvent flows. Larger particles are carried along by the solvent stream and islands with different pigmentation occur. These, so-called, Bénard cells are clearly visible (see Technical Background "Slip and Flow Additives", p. 61).

This unwelcome separation of pigment particles can be prevented if suitable dispersing additives are used to induce controlled flocculation.

## Pigments, dyes and fillers

To understand the complex functions, and therefore the importance, of wetting and dispersing additives in a formulation, one must first examine the complexity of pigments, dyes and fillers.

Pigments and dyes are termed colorants, materials which are used to color other materials. In contrast to dyes, which are soluble in the application medium, pigments consist of particles which are insoluble.

Pigments, dyes and fillers can be natural or synthetic. Traditionally, they are separated into organic and inorganic. Organic pigments and dyes are mainly characterized chemically by their aro-

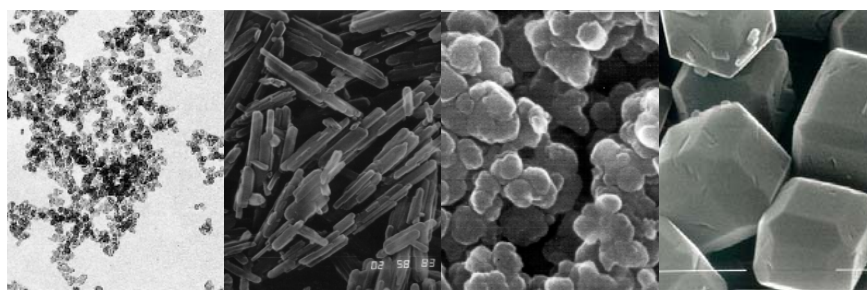


Figure 2: a) carbon black, b)+c) iron oxide yellow, d) magnetic pigment

pictures: a) Degussa, b)-d) Lanxess

matic groups<sup>1</sup>. Inorganic pigments are usually oxides, oxyhydroxides, sulfides, silicates, sulfates or carbonates<sup>2</sup>. Often formulations contain several colorant types. Fillers, like pigments, are insoluble in the application medium. They are mainly used to raise the solids content of the formulation. However they can affect other properties such as the mechanical strength of the paint film.

Pigments are used primarily to impart color. They often contribute to the mechanical properties of the film and im-

prove its weathering and corrosion resistance and its processing properties. Particle sizes of pigments cover a wide range (10 to 1000 nm) but the best range is between 50 and 500 nm. Pigment particles of this size allow optimum values of color strength, purity, gloss, hiding power, lightfastness and weathering resistance to be achieved. As the color properties are directly related to the particle sizes, these must be kept within tight limits to guarantee reliable product properties.

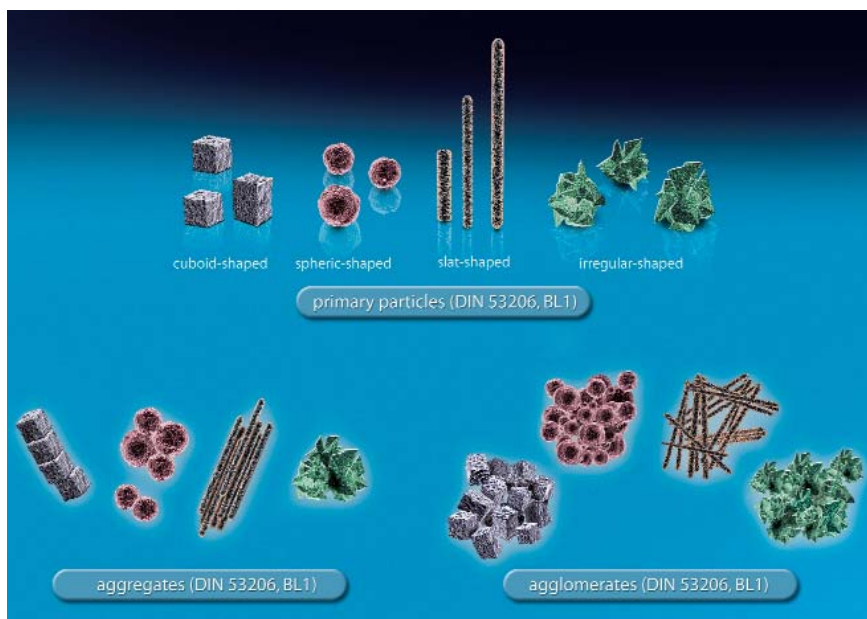


Figure 3: Primary particles, aggregates and agglomerates: grouped according to DIN 53206



The geometric structures and particle shapes of pigments are numerous. Iron oxide occurs as needles, carbon black is paracrystalline, titanium dioxide is almost spherical, barium sulfate is quadrilateral or rhomboid and aluminum bronzes are flakes.

An industrial pigment always exhibits a distribution of particle sizes which affects the wetting behavior. A high proportion of smaller particles needs a higher amount of additive. Under some conditions, very dense spherical packing increases the dispersion time.

Other physical properties, such as electrical charge and magnetism, also have a major effect on the grinding of a pigment. If the surface of the pigment is

modified, the characteristics of the particle change. Crystal lattices of inorganic pigments are sometimes stabilized with foreign ions. The surfaces of organic pigments are already partially treated with surface-active wetting additives.

Just these few general properties of the pigment give some idea of the potential complexity of relationships in a formulation. It is easy to imagine how this complexity can grow when the many influences of the different binders and their polarities are included. To control the associated phenomena, the user must often combine several additives. The additive manufacturer is faced with the challenge of developing multifunctional additives.

## The dispersion process

The dispersion process can be separated into three individual steps which occur both sequentially and consecutively: wetting, dispersion, stabilization.

### Wetting

In order that pigment particles can be finely dispersed in a liquid, the particles must be wetted by the liquid. Air incorporated in the pigment powder must be completely replaced and the pigment particle completely surrounded by liquid. The process of wetting a solid with a liquid can be approximately described by the Young equation:

$$\gamma_s = \gamma_{sl} + \gamma_l \cdot \cos \Theta$$

or

$$\frac{\gamma_s - \gamma_{sl}}{\gamma_l} = \cos \Theta$$

where

$\gamma_s$  = free surface energy of the solid

$\gamma_{sl}$  = solid/liquid boundary surface energy

$\gamma_l$  = surface tension of the liquid

$\Theta$  = contact angle between solid and liquid

With spontaneous wetting or spreading the contact angle is zero so that the cosine term is 1. In this case:

$$\gamma_s - \gamma_{sl} = \gamma_l$$

For the liquid to wet the solid, the surface tension of the former must be less than that of the latter. A liquid with lower surface tension wets pigments better than a liquid with higher surface tension. An additive that promotes wetting must therefore primarily reduce the surface tension. However the interfacial surface tension also has an effect. If an additive reduces the surface tension between liquid and solid phases it also promotes wetting. The additive is adsorbed during wetting onto the surface of the pigment and the pigment particles are encapsulated.

The interactions between pigment particles are thereby reduced and the viscosity of the mill-base is lowered.

### Dispersion

The pigment particles are now wetted by an enclosing binder solution and their surfaces are covered with surface-active additive. The additive reduces the interactions between the pigment particles and thus lowers the viscosity of the mill-base. This permits higher pigment loadings which is of special importance for the mechanical dispersion process. Mill-base formulations which have been optimized in this manner are suitable for

all modern milling equipment, such as dissolvers, pearl mills and triple-roll mills.

In the dispersion process itself the pigment aggregates are destroyed and resolved into primary particles and smaller pigment aggregates. Aggregates cannot generally be broken down because the primary particles are so strongly bound surface-to-surface. Account is taken of this in pigment manufacture and the proportion of aggregates carefully controlled. Their amount can affect the color tone of a pigment.

It is clear from the previous discussion that optimal wetting occurs with a wetting angle of  $\theta = 0$ . The time necessary for dispersion cannot be estimated from the Young equation although this would be interesting for industrial pigment grinding because it affects costs. The wetting of a pigment can be treated as a porous powder bed through which a liquid flows. Physically this powder bed can be envisaged as a bundle of capillaries. A relationship between the distance flowed  $l(t)$  of a liquid front in a porous powder bed as a function of time is shown by the Washburn equation:

$$l(t) = \sqrt{\frac{C \cdot \bar{r} \cdot \gamma_l \cdot \cos \theta}{2\eta} \cdot t}$$

where

$l(t)$  = flow distance of the liquid front

$C$  = pigment-specific constant

$\bar{r}$  = average pore radius of the agglomerate

$\gamma_l$  = surface tension of the liquid phase

$\theta$  = contact angle between pigment and liquid

$\eta$  = dynamic viscosity of the liquid phase

$t$  = time

The pigment-specific constant  $C$  describes the orientation of the microcapillaries within the pigment bed. The liquid medium is characterized by its viscosity and surface tension. Both the pigment surface and the liquid medium affect the contact angle via the interfacial surface tension. The equation shows that generally the flow path of the liquid medium in a pigment powder is larger the smaller the contact angle and this can be achieved by, for example, use of dispersing additives which reduce the surface tension of the liquid.



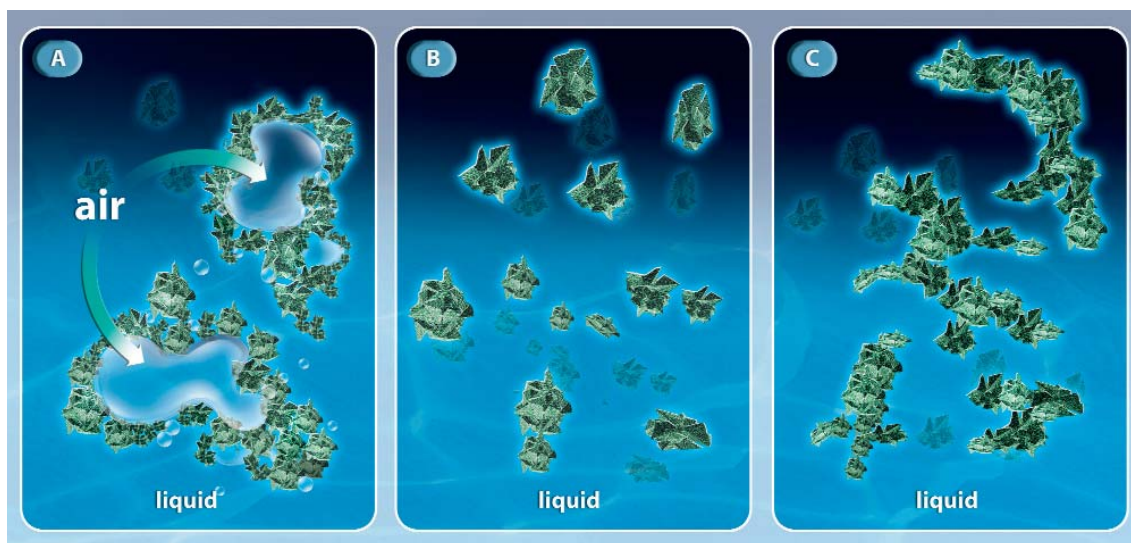


Figure 4: Schematic diagram of (a) agglomerated, (b) dispersed, and (c) flocculated pigments

The lowering of the surface tension is important for another reason. Every dispersion process (breaking up of aggregates and agglomerates) requires input of energy. The work required is calculated from:

$$dW = \gamma \cdot dA$$

where

$W$  = interfacial surface energy

$\gamma$  = surface tension

$A$  = interface area

The equation shows that for an increase in area  $dA$  of the surface during dispersion – by breaking up agglomerates – an energy  $dW$ , proportional to the surface tension  $\gamma$ , is necessary. The smaller the surface tension, the greater the change in surface area for a given amount of dispersion energy. It can equally well be said that for a certain change in surface area in the presence of a dispersion additive – that is with lowered surface tension – less dispersion energy is needed. This is why wetting and dispersion addi-

tives are so important in dispersing processes. They reduce the dispersion time by reduction of the contact angle, as indicated in the Washburn equation, reduce the necessary energy input and prevent re-agglomeration during dispersion.

#### Stabilization

Agglomerates (fig. 4a) are broken down into primary particles and smaller aggregates by the dispersion process. The formation of primary particles is accompanied by an increase of interfacial area with the liquid medium (fig. 4b). The higher the interfacial tension the greater is the driving force for the solid to reduce its interfacial area. This causes the particles to re-agglomerate to form so-called flocculates (fig. 4c). A flocculate is an agglomerate in suspension. Dispersing additives suppress the formation of flocculates.

To stabilize the fine pigment dispersion, the additive molecules must be firmly adsorbed on the pigment surface. This requires the presence of groups or seg-

ments in the additive molecule which can interact strongly with the pigment surface via ionic bonds, dipole interactions or hydrogen bridges. Depending on whether the formulation is water or solventborne, various mechanisms are possible.

In waterborne coatings, electrostatic repulsion has traditionally been regarded as the most important stabilization factor. Interactions within the formulation can be described by the DLVO theory (named after Derjagin, Landau, Verwey and Overbeek). The interplay between the forces of attraction and repulsion must be considered in interpreting the stability of waterborne dispersions. The pigment particles are surrounded by an electrochemical double layer. Each pigment particle is virtually situated in a solution of oppositely charged ions which are relatively firmly attached to the pigment. The strengths of the attracting and repelling forces are a function of the distance between particles. In a strongly pronounced double layer, repulsion predominates and the dispersion is stable.

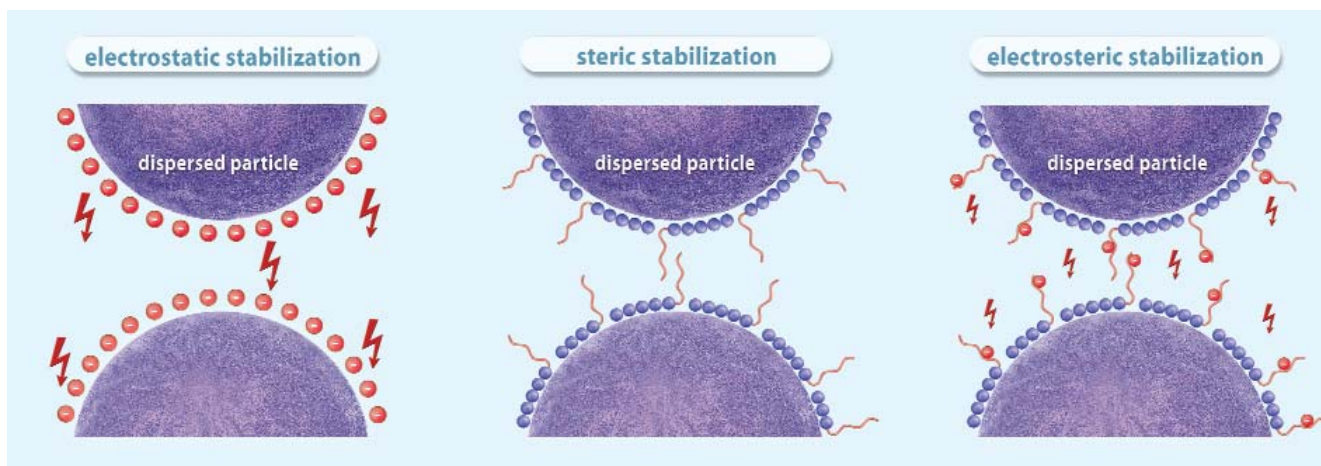


Figure 5: Electrostatic, steric, and electrosteric stabilization of dispersed particles

If the electrochemical double layer is disrupted, by, for example, the addition of electrolyte, the attractive forces gain the upper hand and the dispersion breaks down. The electrostatic interactions can be described quantitatively by the Zeta potential  $\zeta$ , which is a measure of the potential at the shear layer of a moving particle in a dispersion. As  $\zeta$  approaches zero, the tendency of the particles to agglomerate increases. Dispersing additives enlarge the electrochemical double layer thus stabilizing the dispersion.

Solventborne paint systems cannot be stabilized electrostatically. Instead, the preferred way of preventing particle flocculation is by steric stabilization using polymeric additives with groups which have an affinity for pigments. These groups attach themselves to the pigment surface and ensure adsorption of the additive. The polymer segments are responsible for compatibility in the organic system and also stabilize the dispersion by protruding into the solvent. If they come too close the polymer

segments interpenetrate, their mobility is restricted thus lowering the entropy. The pigment particles surrounded by polymer migrate apart again to compensate for this entropy loss.

To enable wetting and dispersing additives to meet the complex demands made on them, it makes sense to combine electrostatic and steric effects. This principle, sometimes called electrosteric

stabilization, is the *modus operandi* of modern wetting and dispersing additives. Only such additives can fulfill the high demands made on stabilization and durability.

Another way of preventing pigment particles approaching each other and thus flocculating is "controlled flocculation". In this process, the structure of the additives causes mutual interaction. The

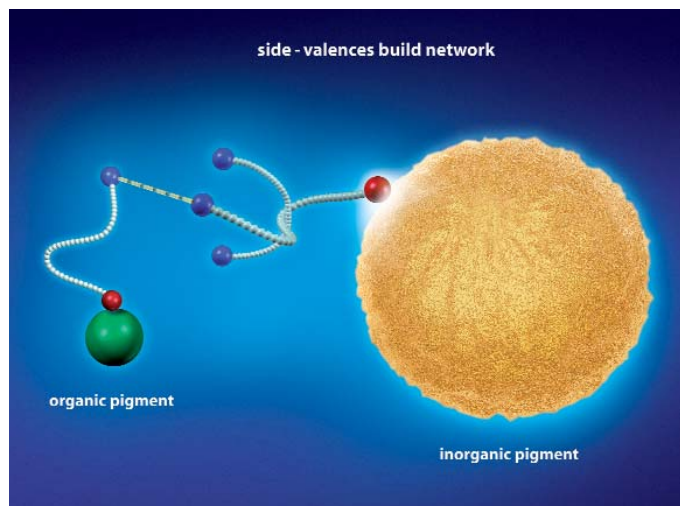


Figure 6: Simplified representation (not to scale) of controlled flocculation by cross-linking of additive molecules



individual additive molecules adsorb on the pigment surface and build a three-dimensional network by interacting. This network results in a change in the rheological properties: in a state of rest the viscosity is very high so that the pigments can no longer easily settle. The differing mobility of the pigments, which is also partly responsible for floating, is prevented by bonding the pigments to flocculates of the same color.<sup>3</sup>

The three-dimensional network can, however, disrupt the flow of the paint and reduce gloss. Controlled flocculation is therefore used primarily in solvent-borne primers and fillers. In waterborne systems, this method is not efficient. Similar characteristics can be achieved with associative thickeners.

## Structure of wetting and dispersing additives

Wetting and dispersing additives are amphiphilic compounds, i.e., they are both hydrophilic and lipophilic. Their molecular structure enables them to enable or promote dispersion of pigments and filling agents in solvents. They should also stabilize the disperse state.

Wetting and dispersing additives can be classified in various ways. In the literature they are classified according to chemical structure or by dividing into ionic and non-ionic products. They may also be grouped according to area of application, i.e. waterborne and non-waterborne, or by pigment type, i.e. organic or inorganic. Molecular size is also a possible criterion whereby wetting additives are defined as low molecular and dispersing additives as high molecular. Because of the complexity of amphiphilic substances, which moreover exhibit unique functions, it is not easy to develop a simple model. The transitions are fluid because the desired

multi-functionality of combinations necessitates various wetting agent components.

One of the factors determining the efficacy of a wetting and dispersing additive is the number of its "anchor groups". With only one single anchor group per dispersing additive molecule, displacement by a solvent molecule leads immediately to complete detachment of the additive molecule from the surface. This would result in flocculation of the pigment. Additives with several functional groups cannot be so easily detached and are particularly high performance (fig. 7).

In organic pigments, aromatic groups are the main chemical structure giving rise to the additive properties. That is why, in the case of organic pigments, dispersing additives which contain, for example, phenyl or naphthyl units are particularly suitable for lasting stabilization of the dispersion.

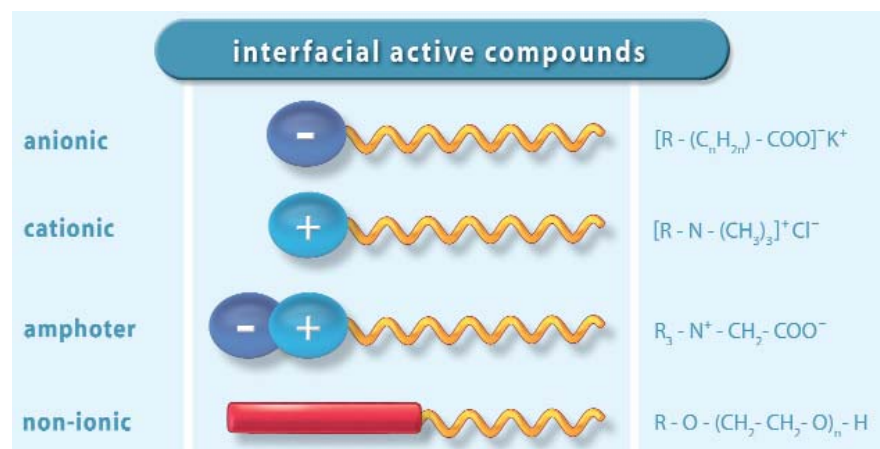


Figure 7: Schematic of the structure of surfactant compounds with various types of head groups

Inorganic pigments can also be divided into chemical classes. These are largely oxides, oxyhydroxides, sulfides, silicates, sulfates or carbonates.<sup>3</sup> These pigments are distinguished by polar molecular structures so that their interactions with acid groups, such as carboxy, phosphate or sulfate groups, are particularly pronounced.

Carbon blacks are a special case. The surface area of such pigments is many times greater than that of organic or even inorganic pigments. On the one hand, this necessitates significantly more dispersing additive to effectively coat a surface; on the other carbon black has neither a classic organic aromatic nor an inorganic crystalline structure. Experience has shown that nitrogen-containing dispersing additives are the most effective.

The structure of oligomeric and polymeric dispersing additives is particularly suitable for steric stabilization. Block and graft polymers are more suitable than homo- or copolymers with a random statistical distribution. Groups with an affinity for pigments are incorporated in the polymer additive to suit the type of pigment and application (fig. 8).

Modern high-performance polymeric wetting and dispersing additives which are suitable for all types of pigment, possess multiple examples of all the above mentioned adhesive groups, e.g. TEGO® Dispers 755 W.

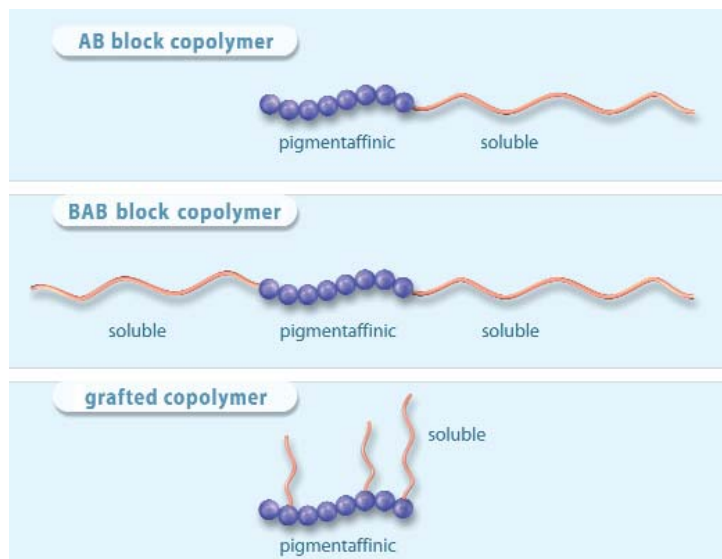


Figure 8: Copolymers for steric stabilization



## Evaluation of wetting and dispersing additives

### Particle size

The prime criterion for the quality of dispersion is particle size distribution. The end point of the dispersion process can be recognized easily by determining the particle size or maximum particle size. The simplest method of measuring the maximum particle size of inorganic pigments is the Grindometer draw down. A sample of the mill-base is painted on a grindometer. Large particles are displaced by a doctor blade and generate stripes in the draw down. The size of the largest particles can be read directly off a scale.

With a little practice, the maximum particle size of the mill-base can be quickly and simply determined using a Grindometer. The particle size distribution cannot, however, be measured in this way. The Grindometer is of no use with binder-free dispersions which dry very rapidly and with particle sizes less than 5  $\mu\text{m}$ .

Very small particles and particle size distributions can be measured by more sophisticated methods such as laser diffraction or ultrasound which are, however, generally unsuitable for routine laboratory practice because of their high operating expense.

It is possible to determine very reliably by indirect means whether the desired particle size has been achieved. For example, the color intensity of organic

pigments is dependent on particle size. The endpoint can be determined by measuring the development of color intensity at intervals during dispersing.

### Color intensity

To determine the color intensity, a sample of the mill-base is let down in a suitable formulation. The result is assessed optically or using a spectrophotometer and compared with that of a standard grind. The amount of mill-base is adjusted until the optical impression given by both samples is the same. The relative color intensity of the sample in % of the standard can be calculated taking into account the various amounts used. This method is very time-consuming but gives meaningful comparative data and is used mainly by pigment manufacturers.

Absolute values can be obtained by a method based on the Kubelka-Munck theory which relates remission to transmission. Summing the remission values over the whole wavelength range gives a value of the color intensity.

In practice, this method suffers from a systematic error since it is based on the assumption of an infinite film thickness and a constant degree of reflection. It is unsuitable for pigment development.



Color intensity according to Kubelka-Munk:

$$FS = \frac{K}{S} = \frac{(1-R)^2}{2R}$$

where

FS: Color strength

K: Coefficient of absorption

S: Coefficient of scattering

R: Reflection at infinite film thickness (hence no change in degree of reflection)

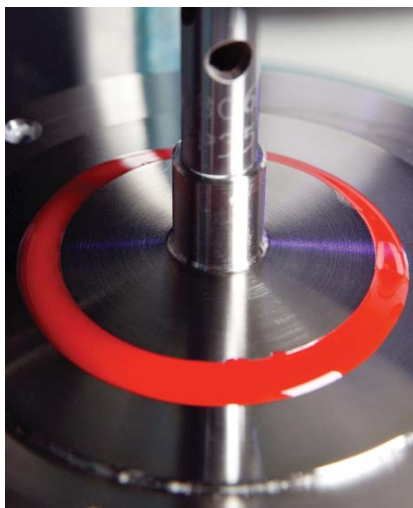
### Rub-out

A rub-out test is suitable for checking stabilization of the pigment particles. It can be used to assess the compatibility of pigment concentrates, the tendency of pigment particles to flocculate and flooding phenomena. An area of the moist but partly dry paint film is rubbed with a finger or brush. If the pigments have demixed or are strongly flocculated, the mechanical process of rubbing re-establishes homogeneous distribution. Viscosity in the dry film has already increased strongly. This stabilizes the pigment particle distribution which is now homogeneous again. The extent of pigment separation or flocculation is recognizable from the color difference from that of the unrubbed film. The color difference is usually quoted as the separation of the chromaticity  $\Delta E$ .  $\Delta E$  is dimensionless. For  $\Delta E$  less than 0.5, no color difference is visible, between 0.5 and 1.0 the color difference is only slightly visible.  $\Delta E$  values greater than 1 are not acceptable.

### Viscosity

The viscosity of a mill-base must be adapted to suit the dispersing unit. If the viscosity of the mill-base is excessive, the unit may be damaged. If it is too low, input of shear forces will be inadequate to break down the pigment agglomerates. Viscosity is also an important indicator of the stability of a pigment concentrate. If it changes during storage, the pigments are usually inadequately stabilized.

The dynamic viscosity of a mill-base can be quickly and easily determined using a Brookfield viscometer. This method can only be used, however, for quality control. Mill-bases exhibit pseudoplastic flow characteristics. Their viscosity change is dependent of the shear energy. A complete flow curve is required to obtain an exact picture of the flow characteristics of a mill-base. This is obtained by measuring the viscosity of the mill-base at different shear rates using a rotational viscometer. Such flow curves



provide information on the flow behavior of the material from manufacture, through transport to application. Interactions in the dispersion can also be quickly detected.

Detailed information on the theory of viscosity and rheology is given in "Technical Background: Rheological Additives"(p. 98).

### What to do if problems still occur

Despite innovative, high performance wetting and dispersing additives, dispersion of pigments is no easy task. Unexpected problems occur frequently especially with waterborne formulations.

We can provide advice and back-up to enable you to exploit the performance of our additives to the full.

#### Literature:

[1] DIN 55987: 1981-02

[2] W. Herbst, K. Hunger, *Industrial Organic Pigments*, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1993, p. 4ff

[3] G. Buxbaum, *Industrial Inorganic Pigments*, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1993, p. 9

## FAQ:

### *Why isn't electrostatic stabilization possible in solventborne formulations?*

A prerequisite for electrostatic stabilization is dissociation of the additive molecules into adsorbed anionic and free mobile cationic components. Even in polar solvents, this dissociation is still only very limited. A double layer cannot therefore form around the pigment particles and electrostatic stabilization is not possible.

### *What are the advantages of combining wetting and dispersing additives with wetting agents?*

Frequently, the terms wetting agent and dispersing agent are erroneously used synonymously. As the name implies, wetting agents are excellently suited for wetting surfaces. In the case of pigment dispersion, they are able to wet the pigment surface very well but are also able to stabilize the finely-dispersed particles. A combination of wetting agent and wetting and dispersing additive can provide the advantages of both classes of additive. The wetting agent is rapid and mobile and promotes penetration of the pigment powder by the liquid thus shortening the wetting and dispersing time. It smoothes the way for the polymeric wetting and dispersing additive which ensures stabilization of the pigment particles.

### *Why do inorganic pigments achieve a higher hiding power than organic pigments?*

Hiding power is an expression of the ability of the coating to prevent light reaching the substrate surface. The small amount which still reaches the surface is absorbed on the return path. Hiding power is largely determined by the degree of light scattering. When passing through the coating, light is deflected so often that it does not reach the substrate surface.

The ability of a substance to refract light is described by the refractive index. The greater the difference between the refractive index of the substance and that of the surrounding medium, the more strongly is the incident light refracted or scattered. The refractive index of inorganic pigments is very high. Organic pigments are known for their ability to absorb light, quantified by a very high specific coefficient of absorption. The wavelengths which are not absorbed are scarcely refracted at all. Coatings with organic pigments thus do not hide as well as those containing inorganic pigments.

### *Can wetting and dispersing additives be added subsequently?*

Wetting and dispersing additives reduce the interfacial surface tension between pigment and water thus improving wetting of the pigment powder. During dispersion, the additive is then anchored to the pigment surface. Such anchoring is necessary to enable the additive to stabilize the fine pigment particles against

flocculation. It is definitely recommended that the wetting and dispersing additive be added before dispersion so that its full effect can be developed.

If the viscosity is lowered sufficiently during dispersion, further additive can be added. As long as the pigment surface is not fully coated, additive molecules can still anchor and carry out their function. Once wetting and dispersing are complete, addition of additive is almost useless.

Post addition of compatibilizers to the finished grind can, however, increase the compatibility of pigment concentrates and the base paint. Even after dispersion, such compatibilizers adsorb on the pigment surface and improve pigment paste uptake and compatibility.

