Wetting and Dispersing Additives
TEGO® Dispers
Optimal dispersion and stabilization of pigment particles is a significant factor in determining the end properties of lacquers, paints or printing inks. The pigments and fillers of the formulation must be ground to small-sized particles, wetted and uniformly distributed as stably as possible. Only then can color intensity, gloss, hiding power, lightfastness and weathering resistance be maximized. Pigment dispersion and stabilization, which requires time and energy, is hardly possible without suitable wetting and dispersing additives.

What occurs during dispersion?

Pigment dispersion can be broken down into three steps which occur partly consecutively and partly concurrently: wetting, dispersion and stabilization.

**Wetting**

Wetting the pigment particles is essential for them to be finely distributed in a liquid. Air entrapped in the pigment powder must be fully removed and the pigment particle completely surrounded by the liquid medium. The processes involved in wetting a solid are 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
- \(\gamma_{sl}\) : interfacial energy solid/liquid
- \(\gamma_l\) : surface tension of the liquid
- \(\theta\) : contact angle solid/liquid

With spontaneous wetting or spreading, the contact angle is zero so that the cosine term is 1. This occurs when:

\[
\gamma_s - \gamma_{sl} = \gamma_l
\]

For the liquid to wet the solid, the surface tension of the liquid must be lower than that of the solid. A liquid with lower surface tension wets pigments better than one with higher surface tension. An additive which promotes wetting must therefore primarily reduce the surface tension of the liquid.
However, wetting and dispersing additives do not only lower the surface tension of the liquid. As their pigment affinic groups cause them to be adsorbed onto the pigment surface, they also alter the boundary surface. The surface tension is no longer that between pigment and liquid but between additive and liquid.

Wetting and dispersing additives lower the surface tension of the liquid and the interfacial tension between pigment and liquid so that wetting is promoted in two ways.

**Dispersion**

The pigment particles are now wetted by the surrounding binder solution and their surface coated with the surface-active additive. The additive reduces the interactions between the pigment particles and lowers the viscosity of the millbase. This allows higher pigment loadings to be achieved, which is particularly important for the mechanical dispersion process. Millbase formulations which have been optimized in this manner are suitable for all modern grinding equipment such as dissolvers, bead mills and three-roll mills.

In the dispersion process itself, the pigment agglomerates are broken up into primary particles and smaller pigment aggregates. Usually aggregates cannot be broken up. The primary particles in aggregates are so strongly bound surface to surface that it is practically impossible to break them apart. Account is taken of this in pigment manufacture and the proportion of aggregates specifically controlled. Their amount can affect the color tone of a pigment.

Every dispersion process to break up aggregates and agglomerates requires energy. The work needed is given by:

\[
dW = \gamma \cdot dA
\]

where

- \( W \): interfacial surface energy
- \( \gamma \): surface tension
- \( A \): interface area

This equation indicates that, for an increase of the surface \( dA \) during dispersion (by breaking up agglomerates), an energy input \( dW \) is needed which is proportional to the surface tension \( \gamma \). The smaller the surface tension, the greater the increase in surface area for a particular amount of energy applied. Equally, for a particular change in surface area in the presence of a dispersing additive (that is at reduced surface tension) less dispersion energy is needed.
Stabilization

In the dispersion process, the aggregates (fig. 1a) are broken up into primary particles and smaller agglomerates. Formation of primary particles results in an increase of the boundary area with the liquid medium (fig. 1b). The higher the interfacial tension, the more strongly will a solid attempt to reduce the interfacial area. The particles, therefore, reagglomerate to form so-called floculates (fig. 1c). The term floculate indicates an agglomerate occurring in suspension. Dispersing additives suppress the formation of floculates.

To stabilize the fine distribution of particles, the additive molecules must be firmly adsorbed onto the pigment surface. This means that the additive molecules require groups or segments which can interact strongly with the pigment surface by ionic bonding, dipole interactions or hydrogen bridges. Depending on whether the formulation is water- or solventborne, various mechanisms are possible.

In waterborne coatings, electrostatic repulsion is traditionally the most important stabilizing factor. Interactions within the formulation can be described by the DLVO-theory (named after Derjagin, Landau, Verwey and Overbeek). In interpreting the stability of waterborne dispersions, the interplay between attractive and repulsive forces is considered.

Dissociation of the adsorbed additive molecules into bound anions and freely moving cations forms an electrochemical double layer around the pigment particles. Each pigment particle is situated in a solution of oppositely charged ions which are relatively firmly bound to the pigment. Both attractive and repulsive forces depend on the interparticle separation. With a strongly pronounced double layer, repulsion predominates and the dispersion is stable. If the electrochemical double layer is disrupted, for example by addition of an electrolyte, attractive forces dominate and the dispersion breaks up. Electrostatic interactions can be qualitatively described 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.

Solventborne paint systems cannot be stabilized electrostatically. Particle floculation is instead preferably prevented by steric stabilization. Polymeric additives with pigment-affinitive groups are used. These groups attach themselves to the pigment surface and thus ensure adsorption of the additive. The polymer segments are responsible for compatibility in organic systems. They also stabilize the dispersion by protruding into the solvent. If the pigment particles come too close, the polymer segments interpenetrate and their mobility is reduced, thus lowering the entropy. The pigment particles surrounded by the polymers move away from each other to balance this entropy loss.

With the complex demands made of wetting and dispersing additives, it is useful to combine electrostatic and steric effects. This is often known as electrosteric stabilization.

Modern wetting and dispersing additives for waterborne application use electrosteric stabilization. Only such additives can fulfill the high demands made on stabilization and durability.

Figure 1: Schematic representation, (a) agglomerated, (b) dispersed, (c) floculated pigments
A further possibility of preventing pigment particles approaching each other and thereby flocculating is "controlled flocculation". In this, the structure of the additives allows them to mutually interact. The individual additive molecules adsorb onto the pigment surface and by interaction with each other form a three-dimensional network. This network causes a change in the rheological properties: at rest, the viscosity is very high so that the pigments can no longer easily precipitate. The different mobility of the pigments, which is also partly responsible for flooding and floating, is prevented by pigments binding to flocculates of the same color (fig. 3).

However, the three-dimensional network can compromise the flow of the coating and thus reduce gloss. Controlled flocculation is therefore mainly used in solventborne primers and fillers. This method is not used for waterborne coatings; a similar effect can be achieved there with associative thickeners.
Wetting and dispersing additives are amphiphilic compounds, i.e. they are both hydrophilic and lipophilic. Their special molecular structure allows them to enable or facilitate dispersion of pigments and fillers in the solvent. In addition, they should stabilize the dispersion.

Wetting and dispersing additives can be classified in different ways. In the literature, there are assignments according to chemical structure or separation into ionic and non-ionic products. Other classifications are made by field of application, waterborne or non waterborne, or by pigment type, organic or inorganic. A classification by molecular size is also possible: wetting agents are of low molecular weight and dispersing additives are of high molecular weight. Because of the complexity of amphiphilic substances, which contain unique functional groups, it is not easy to develop a simple model. The boundaries are not fixed as the desired multifunctionality necessitates deliberate combinations of different wetting agent components.

In principle, every wetting agent has one or more “adhesion groups” which can dock with the pigment and a more-or-less long segment which can be solvated. This general principle is shown in the following simplified schematic diagram:

![Schematic diagram of the structure of surfactant compounds with various types of head groups]

**Structure of wetting and dispersing additives**

Figure 4: Schematic diagram of the structure of surfactant compounds with various types of head groups
The number of adhesion groups is among those properties important for the effectiveness of a wetting and dispersing additive. Adhesion groups are functional groups which have a special affinity for pigment surfaces. If there is only one adhesion group per molecule of dispersing additive, replacement by a solvent molecule leads immediately to complete removal of the additive molecule from the surface. This leads to flocculation of the pigment. Additives with several functional groups cannot so easily be removed and therefore show especially high performance.

The type of adhesion group depends on the particular pigment surface: Organic pigments usually contain aromatic groups so that dispersing additives, which contain, for example, phenyl or naphthyl units, are particularly suitable for long-term stabilization of dispersions. Inorganic pigments can also be split into chemical classes. With a few exceptions these are oxides, oxyhydroxides, sulphides, silicates, sulphates or carbonates. These pigments are characterized by polar molecular structures so that their interaction with acid groups, such as carboxy, phosphate or sulphate, are particularly strong.

Carbon blacks are a special case. The surface area of these pigments is many times greater than that of organic or inorganic pigments. On the one hand, a much larger amount of dispersing additive is needed to cover the surface effectively. On the other hand, carbon black has neither a classic organic/aromatic nor an inorganic/crystalline structure. Experience has shown that nitrogen-containing dispersing additives are the most successful.

Oligomeric and polymeric dispersing additives are particularly suited for steric stabilization. It has been found that block- and graft-copolymers are better than homo- or copolymers with a random statistical distribution. Pigment affinic groups are incorporated in the additive depending on the type of pigment and the application (fig. 5).

Modern high performance polymeric wetting and dispersing additives suitable for all types of pigments have multiple occurrences of all types of adhesion groups, e.g. TEGO® Dispers 755 W.

![Figure 5: Copolymers for steric stabilization](image-url)
The function of wetting and dispersing additives

Wetting and dispersing additives lower the viscosity of a coating formulation. However, that is not their only effect. This class of additives has a marked effect on a whole series of different, essential characteristics of the formulation.

**Color intensity**

The color intensity is a measure of the ability of a pigment to absorb incident light and impart color to a medium. It has practical importance in coloring white base paints: the stronger the color of a tinting agent, the more economical it is. The color intensity of such a preparation depends significantly on the absorbing power and the average particle size of the pigment. The smaller the pigment particles, the greater their effective surface area and consequently the higher their absorbing power. A higher absorbing power is associated with higher color intensity. To ensure that the small pigment particles remain finely distributed and do not clump together to form larger floculates, they must be stabilized. Dispersing additives are necessary for this.

**Hiding power**

The hiding power of a coating is its ability to cover the color or the color difference with the substrate. How well the substrate is hidden depends on the coating thickness, the color of the substrate and on the scattering power of the pigment and the refractive index of the pigment with the surrounding medium (usually the film forming agent). In a coating with strong hiding power, the pigment particles scatter the light so strongly that it hardly reaches the substrate. If residual light is reflected from the substrate, it is so strongly scattered that it does not reach the eye. For a coating to scatter the light optimally, an even, fine distribution of the pigment stabilized by dispersing additives is essential.

**Flocculation**

Flocculation is the reagglomeration of already dispersed particles. In the dispersion process, energy is taken in to break up the pigments and form new surfaces. This is, however, an unstable state and flocculation can occur at any time during manufacturing, storing and applying a paint.
Pigments also tend to flocculate after the paint has been applied to a surface – carbon black with its high surface area is particularly susceptible. If this occurs, a substrate cannot be evenly coated in black. Dispersing additives inhibit flocculation of the pigment particles.

Gloss

Light falling on a surface can be reflected directly (specular reflection) or diffusely. High gloss is obtained when the surface is very smooth and the diffuse component of the reflection is small. Pigment particles or flocculates which protrude from the surface interfere with the specular reflection. Flocculated pigments also affect leveling. Poor leveling decreases the gloss further. Since wetting and dispersing additives inhibit flocculation, they increase the gloss of a coating.

Flooding and floating

These phenomena occur with mixed pigments when the density and/or the particle sizes of the pigments are markedly different.

With its high density, titanium dioxide tends to concentrate at the bottom of the drying paint film. Organic colored pigments have significantly lower density than titanium dioxide and, therefore, concentrate in the upper part of the film.

This vertical flooding, also known as floating, causes the film to appear more colored than desired. Flooding can be made visible by rub-up tests.

Horizontal flooding occurs by separation of the color pigments in the drying film and originates from solvent flows: particles with lower density are entrained with the solvent flow and islands with different pigmentation result. These so-called Bénard cells are clearly visible.

This unwelcome separation of pigment particles can be prevented if they are associated with each other in a controlled manner by suitable dispersing additives which induce controlled flocculation.
Evaluation of wetting and dispersing additives

**Particle size**

The primary criterion which decides the quality of a dispersion is the particle size distribution. By measuring the particle size or the size of the largest particle, the endpoint of a dispersion process can be very well established. The grindometer is the simplest method of measuring the maximum particle size of inorganic pigments. A sample of the millbase is brushed onto a grindometer. Large particles are moved by the doctor blade and produce stripes in the draw down. The size of the largest particles can be read directly from a scale.

With a little practice, the grind gauge allows quick and simple measurement of the maximum particle size. However, the particle size distribution cannot be measured in this way. The grindometer is of no use for binder-free dispersions which dry very quickly or for particle sizes less than 5 μm.

Very small particles and particle size distributions can be studied with more sophisticated measuring methods such as laser diffraction or ultrasound. However, because of their high cost, these methods are generally unsuitable for routine use in the laboratory.
Whether or not the desired particle size has been reached can be easily determined using secondary indices. Thus, with organic pigments, the color intensity is dependent on the particle size. By measuring the color intensity at various times during dispersion, changes in color intensity can be followed and the end point of the dispersion determined.

**Color intensity**

To determine the color intensity, a sample of the millbase is let down in a suitable paint formulation. Assessment is made by comparison with the same amount of a standard millbase optically or using a spectrophotometer. The amount of millbase is adjusted until both samples have the same optical properties. The relative color intensity of the sample as a percentage of the standard is calculated from the various amounts used. This method is very time-consuming but delivers meaningful comparative data and is used mainly by pigment manufacturers.

An absolute value can be obtained by a method based on a theory by Kubelka-Munck, involving the ratio of reflectance and transmission. The sum of the reflectance values over the complete wave range gives a value for the color intensity. In practice, however, this method has a systematic error as it is based on the assumption of an infinite film thickness and a constant degree of reflection. It is not suitable for qualitative assessment of a pigment batch.

Color intensity according to Kubelka-Munck:

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

with
- FS: Color intensity
- K: Absorption coefficient
- S: Scattering coefficient
- R: Reflection at infinite film thickness (no change in the degree of reflection)

**Rub-Up**

The Rub-Up test is used to test the stabilization of pigment particles. It allows the compatibility of pigment concentrates, tendency to flocculation of pigment particles and flooding phenomena to be determined. A part of the wet, but already
drying, film is rubbed with a finger or brush. If the pigment particles have demixed or are strongly flocculated, the mechanical rubbing re-establishes a homogeneous distribution. In a drying film, the viscosity has already increased strongly and the re-established homogeneous distribution of the pigment particles is thereby stabilized. The extent of pigment separation or flocculation is obtained from the color difference between the rubbed and non-rubbed film. The color difference is usually quoted as the separation of the color chromaticity, ΔE, which is dimensionless. If ΔE is less than 0.5, no color difference is visible, between 0.5 and 1.0 the color difference is only slightly visible, but a ΔE larger than 1 is not acceptable.

**Viscosity**

The viscosity of a millbase must be suitable for the dispersion unit. If the millbase viscosity is too high, the unit can be damaged. If it is too low, insufficient shear force will be transferred to break up the pigment agglomerates. Viscosity is also an important indicator of the stability of a pigment concentrate. If it alters during storage, the pigments are usually inadequately stabilized.

The dynamic viscosity of a millbase can be quickly and simply determined using a Brookfield viscometer. This method can, however, only be used for quality control. Millbases show pseudoplastic flow behavior. Changes in their viscosity are dependent on the applied shear energy. To obtain an exact picture of the rheological behavior of a millbase, a complete flow curve must be obtained using a rotational viscometer which can measure the viscosity of the millbase at different shear rates.

Such a flow curve provides information about the rheological behavior of the material from manufacture through transport to application. Interactions in the dispersion can also be quickly detected.

Detailed information about the theoretical basis of viscosity and rheological behavior can be found in "Technical Background: Rheological Additives".

**If problems still occur**

In spite of innovative and high performance wetting and dispersing additives, pigment dispersion is not easy. Unexpected problems often occur especially with waterborne formulations. We will be happy to give help and advice to enable you to utilize the full effectiveness of our additives.

Literature:
1. DIN 55987: 1981-02