1 Wetting and dispersing agents

1.1 Dispersing process

Before the dispersing process is discussed, it would be helpful to characterise pigment particles (Figure 1-1). Small, single crystals which are formed during pigment synthesis are called primary particles. Aggregates are primary particles which grow together via their faces; the dispersing process does not generally separate them. Agglomerates are associates of primary particles and/or aggregates joined by their edges (Figures 1-1 to 1-3).

Figure 1-2 shows a scanning electron micrograph and Figure 1-3 an optical micrograph of pigment Red 3 as a typical example of agglomerates of an organic coloured pigment.

Grinding processes are classified as true size reduction (crushing of primary particles) and deagglomeration (grinding of agglomerates to yield aggregates and/or primary particles). In the coatings sector, dispersing or milling is taken to mean the homogeneous distribution of disperse solid particles (e.g. pigments) in a liquid medium (mostly a solution of binder), i.e. deagglomeration.

As the dispersing of pigments is the most important step in paint manufacturing and is necessary for an understanding of dispersing agents, the underlying process will be discussed here briefly.

During dispersing, adhesive forces (e.g. van der Waals) acting between the pigment particles must be overcome \(^{[1]}\). The purpose of dispersing agents is to stabilise the defloculated pigment dispersions, which were
produced by the dispersing process, for a protracted period of time; i.e. the pigment particles must be prevented from flocculating (see Chapter 1.2) \[2\].

The purpose of the dispersing process is to separate agglomerates. Ideally, the outcome is a dispersion of primary particles and aggregates. In practice, though, it is often only deagglomeration of large agglomerates to smaller ones which occurs \[3\]. Excessive dispersing (leading in extreme cases to crushing of primary particles) should be avoided at all costs, because after-treated pigment surfaces can be damaged and application properties can be impaired (see Chapter 1.4).

Dispersing proceeds in three steps:

- **Wetting** of pigment agglomerates
- **Deagglomeration** of pigment agglomerates
- **Stabilisation** of the resulting dispersion against flocculation (see Chapter 1.2 below)

Pigment agglomerates are wetted in two steps. The liquid phase spreads over their surface and then penetrates the pores or voids, displacing air.
Figure 1-6: Particle size distribution of an organic red pigment in an aqueous binder (blank, \(d_{50} = 1.3 \mu m\); see also Figure 1-8)

Figure 1-7: Particle size distribution of an organic red pigment in an aqueous binder (after 10 minutes’ dispersing, \(d_{50} = 0.51 \mu m\); see also Figure 1-8)
Mechanical deagglomeration of the pigment agglomerates increases the tinting strength of coloured pigments (Figure 1-4) and renders them more economical.

Figure 1-5 shows optical micrographs (transmitted light) of a dispersion of phthalocyanine blue pigment after different dispersing periods; the qualitative decrease in agglomerate size is clearly evident.

Figures 1-6 and 1-7 show the quantitative decrease in agglomerate size with increase in dispersing duration as measured by the particle size distribution. After 10 minutes, the agglomerates have disappeared (Figure 1-7).

1.2 Stabilisation of dispersions

During dispersing, adhesive forces (e.g. van der Waals) acting between the pigment particles must be overcome. Dispersing agents are necessary for stabilising the deflocculated pigment dispersion which was produced by the dispersing process; i.e. flocculation caused by these forces of attraction must be inhibited [2]. It is essential to distinguish between the terms dispersing agent and dispersion medium. A dispersing agent is an additive which improves the stability of pigment dispersions whereas a dispersion medium is a liquid phase wherein pigments are dispersed.

Flocculation is the association of pigment particles, which have been dispersed in a liquid paint medium, and is the result of forces of attraction (e.g. van der Waals) between the particles. Flocculation reduces the size of the phase boundary between pigment and dispersion medium. Most disperse systems are thermodynamically unstable, resulting in a decreased interfacial surface area due to flocculation [3]. Why?

The work (energy input) needed to move a molecule from inside a phase to the surface is calculated by:

\[ W = \gamma \cdot \Delta A \]

where

- \( W \) is the work [energy]
- \( \gamma \) is the surface tension [force/length = energy/area] [3]
- \( \Delta A \) is the increase in interfacial area [area]
The work $W$ is proportional to the increase in interfacial area $\Delta A$ and to the surface tension $\gamma$. Consequently, the larger the interfacial area and the higher the surface tension, the higher is the energy content of the disperse system and the less thermodynamically stable it is. Flocculation lowers the energy content of a disperse system because the interfacial area $\Delta A$ decreases; i.e. it shifts the disperse system towards a thermodynamically stable state (Figure 1-9).

Pigment and polymer dispersions are often stable for years because they are metastable. The term metastability is illustrated in Figure 1-9.

So, why do pigment dispersions have a long shelf life, i.e. why they are metastable? The answer is that electrostatic or steric stabilisation can prevent them from flocculating. These terms are explained below. The combination of both these stabilisation mechanisms is called electrosteric stabilisation.

Stabilisation is a kinetic effect. Transformation into the thermodynamically stable state by flocculation is prevented or retarded by a high energy of activation (Figure 1-9).

### 1.2.1 Electrostatic stabilisation

Inorganic pigments and fillers dispersed in water especially (which has a high dielectric constant) mostly bear electric charges. Since the overall disperse system is uncharged, the liquid phase must contain an equal number of counter ions in close proximity to the particles (Figure 1-10). An electric double layer (ion cloud) forms and flocculation is prevented because of the electrostatic repulsion of like charges (this is known as electrostatic stabilisation) [3].
It is important for the forces of repulsion (Coulomb’s law) to extend further into the dispersion medium than the forces of attraction (van der Waals forces; Figure 1-10). Wherever there are opposite charges (e.g. in the case of different pigments), co-flocculation occurs because of electrostatic attraction.

Adding electrolytes (salts) causes the electric double layer (ion cloud) to contract and may lead to flocculation [3].

The Schulze-Hardy law describes how the ionic charge of added salts influences their flocculating power:

- In negatively charged dispersions (the most common), the flocculating power of cations increases with increase in cationic charge: $\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}$ or $\text{Fe}^{3+}$
- In positively charged dispersions (rare, e.g. cathodic electrodeposition primers), the flocculating power of anions increases with increase in anionic charge: $\text{Cl}^– < \text{SO}_4^{2–} < \text{PO}_4^{3–}$

In practice, therefore, waterborne paints should not contain any electrolytes (salts).

There are various mechanisms by which the surfaces of pigment or filler particles can acquire charges:

- Dissociation of functional groups on the particle surfaces
- Adsorption of ions (mostly polyanions); see dispersing agents (Chapter 1.3.1)

**Dissociation of functional groups on particle surfaces**

Oxides have hydroxyl groups on their surfaces [3] that may react as acids or bases, in accordance with the oxide concerned. The pH at which the surface charge is zero (point of zero charge) is also called the isoelectric point (IEP) [4]. Above the IEP, the oxide surface is negatively charged due to deprotonation while, below the IEP, it is positively charged due to protonation [3]. The charge density increases with increase in distance between the pH of the dispersion medium and the IEP.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>IEP (pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>12.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9</td>
</tr>
<tr>
<td>ZnO</td>
<td>9</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>7</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>6.5</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6.7</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>4.5 to 6.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2</td>
</tr>
</tbody>
</table>

The data shown in Table 1-1 apply to chemically pure oxides. There may be significant deviations from these IEP values in the case of industrial pigments or fillers whose surfaces have been after-treated (e.g. titanium dioxide; see Chapter 1.4.2). The type of crystalline structure, too, can influence the IEP.

Electrostatic stabilisation is especially important in waterborne paints and latex paints because of the
high dielectric constant of water. However, studies have shown that the electric charge on pigment surfaces also plays an important role in solventborne paints [6]; the same pigment dispersed in different paint resins may exhibit opposite charges or none at all.

1.2.2 Steric stabilisation

It has been known for more than 100 years that aqueous dispersions (colloids) can be readily stabilised against flocculation by adding water-soluble polymers (so-called protective colloids), such as gelatin, casein, and polyvinyl alcohol. In contrast to electrostatic stabilisation, stabilisation effected with polymers is insensitive to the addition of electrolytes (salts).

As a rule, adding suitable polymers is the only way to stabilise dispersions in organic solvents. The polymers (oligomeric dispersing agents or paint resins) must adsorb on the surface of the dispersed particles; i.e. they must displace adsorbed solvent and/or surfactant molecules.

As pigment particles approach each other, the polymer segments become restricted in their movement and the entropy decreases; the outcome is a repulsive force (Figure 1-11). For this reason, steric stabilisation is also referred to as entropic repulsion or deflocculation.

Studies [7, 8] have shown that, for steric stabilisation of dispersed particles up to 10 µm (10,000 nm) in diameter, the steric barrier need only be 10 nm (Figure 1-12).

The diagram in Figure 1-11 suggests that surfactants (wetting agents) can also act as steric stabilisers (especially if it is not realised that Figure 1-11 is not to scale). Low-molecular surfactants (wetting agents) do not act as steric stabilisers as their molecules are much too small (see Chapter 1.3.2). Only oligomers or polymers have the necessary molecular size.
Requirements for steric stabilisation

a) The polymers must strongly adsorb on the pigment surface by appropriate functional groups (anchoring groups).

b) The polymers must have sufficiently long chain segments (barrier groups) which readily dissolve in the dispersion medium (organic solvents or water), a process that leads to widening of polymer chains. The addition of poor solvents can cause these polymer chains to coil and so lead to flocculation (see “Dispersing agents” in Chapter 1.3.1).

c) Polymers (oligomers) of medium molar mass are optimal:
   • If the molar mass is too low, the chain is not long enough.
   • If the molar mass is too high, bridging flocculation may occur (see “Dispersing agents” in Chapter 1.3.1). Moreover, if the molar mass is too high, incompatibility may occur or the viscosity may increase.

d) A minimum polymer concentration is necessary; if the concentration is too low, flocculation may occur, especially in the case of high molar masses (see c).

1.3 Typical wetting and dispersing agents

Unfortunately, manufacturers provide hardly any information about the chemical composition of their wetting and dispersing agents, and that makes it difficult to explain the effectiveness of these additives. Moreover, they often employ the terms wetting and dispersing agents indiscriminately because the distinction between them is fuzzy.

In this book, they were distinguished by molar mass:

• Wetting agents (surfactants) are low-molecular amphiphilic substances.
• Dispersing agents are oligomers or polymers which stabilise dispersions of pigments and fillers against flocculation.

Let us look at dispersing agents first.

1.3.1 Dispersing agents

Polyanionic dispersing agents for electrostatic stabilisation

Polyanions serving as dispersing agents or dispersing additives adsorb primarily on inorganic pigment and filler surfaces, which they charge by means of their own electric charges.

The purpose of such polyanionic dispersing agents is to increase the level of repulsion and, therefore, to improve electrostatic stabilisation.
Typical wetting and dispersing agents

They achieve this by:
• Boosting the ‘like’ charge
• Reversing the charge of oppositely charged pigments (prevention of co-flocculation)
• Complexing multivalent cations (e.g. Ca\(^{2+}\); thereby increasing the radius of action of electrostatic forces)

Typical polyanionic dispersing agents are polycarboxylates (mostly salts of polyacrylic acids; Figure 1-13).

Figure 1-14 schematically shows the adsorption of a salt of polyacrylic on zinc oxide (IEP at pH 9).

Advantages of polycarboxylates
+ Hydrolytic resistance
+ Similarity to paint resins (compatibility, film quality)

Disadvantages of polycarboxylates
– Higher cost (compared to polyphosphates)
– Sensitive to multivalent cations
– Relatively high addition level.

Further examples of polyanionic dispersing agents are polyphosphates
• Linear polyphosphates:
  \( \text{Na}_{n+2}\text{P}_n\text{O}_{3n+1} \) (Calgon)
  \( n = 2 \): pyrophosphate \( \text{Na}_4\text{P}_2\text{O}_7 \)
  \( n = 4 \): tetraphosphate \( \text{Na}_6\text{P}_4\text{O}_{13} \)
• Cyclic metaphosphates: \( (\text{NaPO}_3)_n \)

The charge and, therefore, the dispersing efficiency increase with increase in \( n \).

Advantages of polyphosphates
+ Lower cost (compared to polycarboxylates)
+ Complexing of multivalent cations (e.g. Ca\(^{2+}\))
+ Relatively low addition level (0.2 to 0.5 wt.%)

Figure 1-13: Salt of a polyacrylic acid as a dispersing agent for waterborne paints

Figure 1-14: Charging of zinc oxide pigment at pH 9 by a polyacrylic acid salt (simplified diagram, not to scale)