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Colloids in Paints

Paints or surface coatings are complex, multi-phase, colloidal systems that are applied as a continuous layer to a surface [1]. A paint usually contains pigmented materials to distinguish it from clear films that are described as lacquers or varnishes. The main purpose of a paint or surface coating is to provide aesthetic appeal and to protect the surface. For example, a motor car paint can enhance the appearance of the car body by providing color and gloss and it also protects the car body from corrosion.

When considering a paint formulation, one must know the specific interaction between the paint components and substrates. This subject is of particular importance when one considers the deposition of the components on the substrate and their adhesion to it. The substrate can be wood, plastic, metal, glass, etc. The interaction forces between the paint components and the substrate must be considered when formulating any paint. In addition, the method of application can vary from one substrate and another.

For many applications, it has been recognized that achieving a required property, such as durability, strong adhesion to the substrate, opacity, color, gloss, mechanical properties, chemical resistance and corrosion protection, requires the application of more than one coat. The first two or three coats (referred to as the primer and undercoat) are applied to seal the substrate and provide strong adhesion to the substrate. The topcoat provides the aesthetic appeal such as gloss, color and smoothness. This clearly explains the complexity of paint systems, which require a fundamental understanding of the processes involved such as particle–surface adhesion, colloidal interaction between the various components and mechanical strength of each coating.

The main objective of the present text is to consider the colloidal phenomena involved in a paint system, its flow characteristics or rheology, its interaction with the substrate and the main criteria that are needed to produce a good paint for a particular application.

To obtain a fundamental understanding of the above basic concepts, one must first consider the paint components. Most paint formulations consist of disperse systems (solid in liquid dispersions). The disperse phase consists of primary pigment particles (organic or inorganic), which provide the opacity, color and other optical effects. These are usually in the submicron range. Other coarse particles

(mostly inorganic) are used in the primer and undercoat to seal the substrate and enhance adhesion of the topcoat. The continuous phase consists of a solution of polymer or resin which provides the basis of a continuous film that seals the surface and protects it from the outside environment. Most modern paints contain latexes, which are used as film formers. These latexes (with a glass transition temperature mostly below ambient temperature) coalesce on the surface and form a strong and durable film. Other components may be present in the paint formulation such as corrosion inhibitors, driers and fungicides.

This introductory chapter gives a brief account of the properties of the main components in a paint formulation, namely the disperse particles and the medium in which they are dispersed (the film formers and the solvent).

1.1
The Disperse Particles

The primary pigment particles (normally in the submicron range) are responsible for the opacity, color and anti-corrosive properties. The principal pigment in use is titanium dioxide due to its high refractive index, and is the one that is used to produce white paint. To produce maximum scattering, the particle size distribution of titanium dioxide has to be controlled within a narrow limit. Rutile, with a refractive index of 2.76, is preferred over anatase, which has a lower refractive index of 2.55. Thus, rutile gives the possibility of higher opacity than anatase and it is more resistant to chalking on exterior exposure. To obtain maximum opacity, the particle size of rutile should be within the range 220–140 nm. The surface of rutile is photoactive and it is surface coated with silica and alumina in various proportions to reduce its photoactivity.

Colored pigments may consist of inorganic or organic particles. For a black pigment, one can use carbon black, copper carbonate, manganese dioxide (inorganic) and aniline black (organic). For yellow, can use lead, zinc, chromates, cadmium sulfide, iron oxides (inorganic) and nickel azo yellow (organic). For blue–violet, one can use ultramarine, Prussian blue, cobalt blue (inorganic), phthalocyanine, indanthrone blue and carbazole violet (organic). For red, one can use red iron oxide, cadmium selenide, red lead, chrome red (inorganic), toluidine red and quinacridones (organic).

The color of a pigment is determined by the selective absorption and reflection of the various wavelengths of visible light (400–700 nm) which impinges on it. For example, a blue pigment appears so because it reflects the blue wavelengths in the incident white light and absorbs the other wavelengths. Black pigments absorb all the wavelengths of incident light almost totally, whereas a white pigment reflects all the visible wavelengths.

The primary shape of a pigmented particle is determined by its chemical nature, its crystalline structure (or lack of it) and the way in which the pigment is created in Nature or made synthetically. Pigments as primary particles may be

spherical, nodular, needle- or rod-like or plate like (lamellar) as illustrated in Figure 1.1.

The pigments are usually supplied in the form of aggregates (whereby the particles are attached at their faces) or agglomerates (where the particles are attached at their corners). When dispersed in the continuous phase, these aggregates and agglomerates must be dispersed into single units. This requires the use of an effective wetter/dispersant and application of mechanical energy. This process of dispersion is discussed in detail in Chapter 3.

In paint formulations, secondary pigments are also used. These are referred to as extenders, fillers and supplementary pigments. They are relatively cheaper than the primary pigments and they are incorporated in conjunction with the primary pigments for a variety of reasons, such as cost effectiveness, enhancement of adhesion, reduction of water permeability and enhancement of corrosion resistance. For example, in a primer or undercoat (matt latex paint), coarse particle extenders such as calcium carbonate are added in conjunction with TiO_2 to achieve whiteness and opacity in a matt or semi-matt product. The particle size of extenders range from submicron to a few tens of microns.

Their refractive index is very close to that of the binder and hence they do not contribute to the opacity from light scattering. Most extenders used in the paint industry are naturally occurring materials such as barytes (barium sulfate), chalk (calcium carbonate), gypsum (calcium sulfate) and silicates (silica, clay, talc or mica). However, more recently synthetic polymeric extenders have been designed to replace some of the TiO_2. A good example is spindrift, which is polymer beads that consist of spherical particles (up to 30 μm in diameter) which contain submicron air bubbles and a small proportion of TiO_2. The small air bubbles (<0.1 μm) reduce the effective refractive index of the polymer matrix, thus enhancing the light scattering of TiO_2.

The refractive index of any material (primary or secondary pigment) is a key to its performance. As is well known, the larger the difference in refractive index between the pigment and the medium in which it is dispersed, the greater is the opacity effect. A summary of the refractive indices of various extender and opacifying pigments is given in Table 1.1.

The refractive index of the medium in which the pigment is dispersed ranges from 1.33 (for water) to 1.4–1.6 (for most film formers). Thus rutile will give the highest opacity, whereas talc and calcium carbonate will be transparent in fully bound surface coatings. Another important fact that affects light scattering is the particle size, and to obtain the maximum opacity from rutile an optimum particle
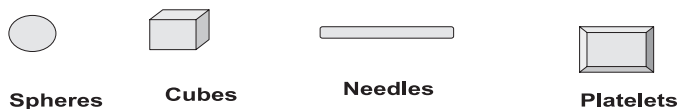

Spheres   **Cubes**   **Needles**   **Platelets**

Figure 1.1 Schematic representation of particle shape.

Table 1.1 Refractive indices (RI) of extenders and opacifying pigments.

Extender pigment	RI	Opacifying white pigment	RI
Calcium carbonate	1.58	Zinc sulfide/Barium sulfate	1.84
China clay	1.56	Zinc oxide	2.01
Talc	1.55	Zinc sulfide	2.37
Barytes	1.64	TiO$_2$ anatase	2.55
		TiO$_2$ rutile	2.76

size of 250 nm is required. This explains the importance of good dispersion the powder in the liquid, which can be achieved by a good wetting/dispersing agent and also application of sufficient milling efficiency.

For colored pigments, the refractive index of a pigment in the non-absorbing or highly reflecting part of the spectrum affects its performance as an opacifying material. For example, Pigment Yellow 1 and Arylamide Yellow G give lower opacity than Pigment Yellow 34 Lead Chromate. Most suppliers of colored pigments attempt to increase the opacifying effect by controlling the particle size.

The nature of the pigment surface plays a very important role in its dispersion in the medium and its affinity to the binder. For example, the polarity of the pigment determines its affinity for alkyds, polyesters, acrylic polymers and latexes that are commonly used as film formers (see below). In addition, the nature of the pigment surface determines its wetting characteristics in the medium in which it is dispersed (which can be aqueous or non-aqueous) and also the dispersion of the aggregates and agglomerates into single particles. It also affects the overall stability of the liquid paint. Most pigments are surface treated by the manufacturer to achieve the optimum performance. As mentioned above, the surface of rutile particles is treated with silica and alumina in various proportions to reduce its photoactivity. If the pigment has to be used in a non-aqueous paint, its surface is also treated with fatty acids and amines to make it hydrophobic for incorporation in an organic medium. This surface treatment enhances the dispersibility of the paint, its opacity and tinting strength and its durability (glass retention, resistance to chalking and color retention). It can also protect the binder in the paint formulation.

The dispersion of the pigment powder in the continuous medium requires several processes, namely wetting of the external and internal surface of the aggregates and agglomerates, separation of the particles from these aggregates and agglomerates by application of mechanical energy, displacement of occluded air and coating of the particles with the dispersion resin. It is also necessary to stabilize the particles against flocculation by either electrostatic double-layer repulsion and/or steric repulsion. The process of wetting and dispersion of pigments is described in detail in Chapter 3 and colloid stability (lack of aggregation) is discussed in Chapter 4.

1.2
The Dispersion Medium and Film Formers

The dispersion medium can be aqueous or non-aqueous, depending on the application. It consists of a dispersion of the binder in the liquid (which is sometimes referred to as the diluent). The term solvent is frequently used to include liquids that do not dissolve the polymeric binder. Solvents are used in paints to enable the paint to be made and they allow application of the paint to the surface. In most cases, the solvent is removed after application by simple evaporation, and if the solvent is completely removed from the paint film it should not affect the paint film performance. However, in the early life of the film solvent retention, it can affect hardness, flexibility and other film properties. In water-based paints, the water may act as a true solvent for some of the components, but it should be a non-solvent for the film former. This is particularly the case with emulsion paints.

With the exception of water, all solvents, diluents and thinners used in surface coatings are organic liquids with low molecular weight. Two types can be distinguished, hydrocarbons (both aliphatic and aromatic) and oxygenated compounds such as ethers, ketones, esters and ether alcohols. Solvents, thinners and diluents control the flow of the wet paint on the substrate to achieve a satisfactory smooth, even, thin film, which dries in a predetermined time. In most cases, mixtures of solvents are used to obtain the optimum condition for paint application. The main factors that must be considered when choosing solvent mixtures are their solvency, viscosity, boiling point, evaporation rate, flash point, chemical nature, odor and toxicity.

The solvent power or solvency of a given liquid or mixture of liquids determines the miscibility of the polymer binder or resin. It has also a large effect on the attraction between particles in a paint formulation, as discussed in detail in Chapter 4. A very useful parameter that describes solvency is the Hildebrand solubility parameter, δ [2, 3], which is related to the energy of association of molecules in the liquid phase in terms of 'cohesive energy density'. The latter is simply the ratio of the energy required to vaporize 1 cm^3 of liquid, ΔE_v, to its molar volume, V_m. The solubility parameter δ is simply the square root of that ratio,

$$\delta = \frac{\Delta E_v}{V_m} \tag{1}$$

Liquids having similar values of δ are miscible, whereas those with a significant difference are immiscible. The solubility parameters of liquids can be determined experimentally by measuring the energy of vaporization. For polymers, one can determine the solubility parameter using an empirical approach by contacting the polymer with liquids with various δ values and observing whether or not dissolution occurs. The solubility parameter of the polymer is taken the average of two δ values for two solvents that appear to dissolve the polymer. A better method is to calculate the solubility parameter from the 'molar attraction constant', G, of

the constituent parts of the molecule [4]:

$$\delta = \frac{\rho \Sigma G}{M} \tag{2}$$

where ρ is the density of the polymer and M is its molecular weight.

Hansen [5] extended Hildebrand's concept by considering three components for the solubility parameter, a dispersion component δ_d, a polar component δ_p and a hydrogen bonding component δ_h:

$$\delta^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2 \tag{3}$$

Values of δ and its components are tabulated in the book by Barton [4].

As mentioned above, the dispersion medium consist of a solvent or diluent and the film former. The latter is also sometimes referred to as a 'binder', since it functions by binding the particulate components together, and this provides the continuous film-forming portion of the coating. The film former can be a low molecular weight polymer (oleoresinous binder, alkyd, polyurethane, amino resin, epoxide resin, unsaturated polyester), a high molecular weight polymer (nitrocellulose, solution vinyls, solution acrylics), an aqueous latex dispersion [poly(vinyl acetate), acrylic, styrene–butadiene] or a non-aqueous polymer dispersion (NAD). This introductory chapter only briefly describes film formers based on polymer solutions. The subject of polymer latexes and non-aqueous dispersions is dealt with in Chapter 2. The polymer solution may exist in the form of a fine particle dispersion in a non-solvent. In some cases, the system may be a mixed solution–dispersion, implying that the solution contains both single polymer chains and aggregates of these chains (sometimes referred to as micelles). A striking difference between a polymer that is completely soluble in the medium and one that contains aggregates of that polymer is the viscosity reached in the two cases. A polymer that is completely soluble in the medium will show a higher viscosity at a given concentration compared with another polymer (at the same concentration) that produces aggregates. Another important difference is the rapid increase in the solution viscosity with increase in molecular weight for a completely soluble polymer. If the polymer makes aggregates in solution, an increase in the molecular weight of the polymer does not give a dramatic increase in viscosity.

The earliest film-forming polymers used in paints were based on natural oils, gums and resins. Modified natural products are based on cellulose derivatives such as nitrocellulose, which is obtained by nitration of cellulose under carefully specified conditions. Organic esters of cellulose such as acetate and butyrate can also be produced. Another class of naturally occurring film formers are those based on vegetable oils and their derived fatty acids (renewable resource materials). Oils used in coatings include linseed oil, soya bean oil, coconut oil and tall oil. When chemically combined into resins, the oil contributes flexibility and,

with many oils, oxidative cross-linking potential. The oil can also be chemically modified, as for example by the hydrogenation of castor oil, which can be combined with alkyd resins to produce some specific properties of the coating.

Another early binder used in paints is the oleoresinous vehicles produced by heating together oils and either natural or certain preformed resins, so that the resin dissolves or disperses in the oil portion of the vehicle. However, these oleoresinous vehicles were later replaced by alkyd resins, which probably constitute of the first applications of synthetic polymers in the coating industry. These alkyd resins are polyesters obtained by reaction of vegetable oil triglycerides, polyols (e.g. glycerol) and dibasic acids or their anhydrides. These alkyd resins enhance the mechanical strength, drying speed and durability over and above those obtained using the oleoresinous vehicles. The alkyds were also modified by replacing part of the dibasic acid with a diisocyanate (such as toluene diisocyanate) to produce greater toughness and quicker drying characteristics.

Another type of binder is based on polyester resins (both saturated and unsaturated). These are typically composed mainly of co-reacted di- or polyhydric alcohols and di- or tribasic acids or acid anhydrides. They have also been modified using silicone to enhance their durability.

More recently, acrylic polymers have been used in paints due to their excellent properties of clarity, strength and chemical and weather resistance. Acrylic polymers refer to systems containing acrylate and methylacrylate esters in their structure along with other vinyl unsaturated compounds. Both thermoplastic and thermosetting systems can be made; the latter are formulated to include monomers possessing additional functional groups that can further react to give cross-links following the formation of the initial polymer structure. These acrylic polymers are synthesized by radical polymerization. The main polymer-forming reaction is a chain propagation step which follows an initial initiation process. A variety of chain transfer reactions are possible before chain growth ceases by a termination process.

Radicals produced by transfer, if sufficiently active, can initiate new polymer chains where a monomer is present that is readily polymerized. Radicals produced by chain transfer agents (low molecular weight thiols, e.g. primary octane-thiol) are designed to initiate new polymer chains. These agents are introduced to control the molecular weight of the polymer.

The monomers used for preparation of acrylic polymers vary in nature and can generally be classified as 'hard' (such as methyl methacrylate, styrene and vinyl acetate) or 'soft' (such as ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate). Reactive monomers may also have hydroxyl groups (such as hydroxyethyl acrylate). Acidic monomers such as methacrylic acid are also reactive and may be included in small amounts in order that the acid groups may enhance pigment dispersion. The practical coating systems are usually copolymers of 'hard' and 'soft'. The polymer hardness is characterized by its glass transition temperature, T_g. The $T_g(K)$ of the copolymer can be estimated from the T_g values of the individual components of the homopolymers with weight fractions W_1 and W_2:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$ (4)

Most acrylic polymers consist of random copolymers. By controlling the proportion of 'hard' and 'soft' monomers and the molecular weight of the final copolymer, one arrives at the right property that is required for a given coating. As mentioned above, two types of acrylic resins can be produced, namely thermoplastic and thermosetting. The former find application in automotive topcoats, although they suffer from some disadvantages such as cracking in cold conditions, which may require a process of plasticization. These problems are overcome by using thermosetting acrylics, which improve the chemical and alkali resistance. Also, it allows one to use higher solid contents in cheaper solvents. Thermosetting resins can be self-cross-linking or may require a co-reacting polymer or hardener.

1.3
Deposition of Particles and Their Adhesion to the Substrate

In a paint film, the pigment particles need to undergo a process of deposition to the surfaces (which is governed by long-range forces such as van der Waals attraction and electrical double-layer repulsion or attraction). This process of deposition is also affected by polymers (nonionic, anionic or cationic) which can enhance or prevent adhesion. Once the particles reach the surface, they have to adhere strongly to the substrate. This process of adhesion is governed by short-range forces (chemical or non-chemical). The same applies to latex particles, which also undergo a process of deposition, adhesion and coalescence. The subject of particle deposition and adhesion is discussed in detail in Chapter 5.

1.4
Flow Characteristics (Rheology) of Paints

Control of the flow characteristics of paints is essential for their successful application. All paints are complex systems consisting of various components such as pigments, film formers, latexes and rheology modifiers. These components interact with each other and the final formulation becomes non-Newtonian, showing complex rheological behavior. The paint is usually applied in three stages, namely transfer of the paint from the bulk container, transfer of the paint from the applicator (brush or roller) to the surface to form a thin, even film and flow-out of film surface, coalescence of polymer particles (latexes) and loss of the medium by evaporation. During each of these processes, the flow characteristics of the paint and its time relaxation produce interesting rheological responses. To understand the rheological behavior of a paint system, one must start with a basic knowledge of rheology. This is described in Chapter 6, which gives an account of the basic principles of rheology. Chapter 7 describes the rheology of suspensions and emul-

sions, which are main components of the paint formulation. Chapter 8 is devoted to the subject of rheology modifiers, which are essential components of a paint formulation. These modifiers are introduced for various reasons, such as maintenance of the long-term stability of the paint, ease of its application and the final characteristics of the film produced. The final chapter gives a brief account of the main rheological characteristics of a paint formulation.

References

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