Seven

Paint

first principles

In this chapter, we describe the basic nature of paint, making clear its function, and describe the various routes to attaining the final properties we require.

Wet paint: paint in the can

All objects are most vulnerable at their surfaces. It is the surface of any article that makes continual contact with the air, which may be moist, corroding or oxidizing. The surfaces of objects left in the open bear the brunt of the sun, rain, fog, dew, ice and snow. Under these conditions iron rusts, wood rots (or shrinks and cracks) and road surfaces crack and disintegrate. These, and more sheltered objects, suffer the wear of daily use, scratches, dents and abrasions — at their surfaces. To prevent or to minimize damage, various coatings are applied to these surfaces to protect them. Coatings can also be used to decorate the articles, to add colour and lustre and to smooth out any roughness or irregularities caused by the manufacturing process. Thus the function of any surface coating is twofold: to protect and to decorate.

There are many surface coatings that do this: wallpaper, plastic sheet, chrome and silver plating. No coating material is more versatile than paint, which can be applied to any surface, however awkward its shape or size, by one process or another. Paint is a loosely used word covering a whole variety of materials, with names sometimes more descriptive of their composition or function: enamels, lacquers, varnishes, undercoats, surfacers, primers, sealers, fillers, stoppers and many others. It is essential to grasp at once that these and other less obviously related products, such as plasters, concrete, tars and adhesives, are all formulated on the same basic principles and contain some or all of three main ingredients.

First a pigment may be included. Pigments have both decorative and protective properties. The simplest form of paint is whitewash and, when dry, whitewash is nothing more than a pigment — whiting (calcium carbonate) — spread over a surface. It decorates and to some extent it
protectors, but it rubs off. So most paints contain the second ingredient, the film-former or binder, which will be a resin or polymer, to bind together the pigment particles and hold them on the surface. If the pigment is left out, the film-former covers and protects the surface, decorating it by giving it gloss or ‘sheen’. It is difficult to attach coatings that are not fluid to any but the simplest of surfaces: those that are flat or gently curving. The fluidity of paint permits penetration into the most intricate crevices. It is achieved by dissolving the film-former in a solvent, or by colloidal suspension of both pigment and film-former in a diluent. Thus the third basic ingredient of paint is a liquid. Often the film-former–liquid mixture is called the vehicle for the pigment.

If the pigment is omitted, the material is usually called a varnish. The term clearcoat is used for unpigmented coatings applied over metallic paints. The pigmented varnish – the paint – is sometimes called an enamel, lacquer, finish or topcoat, meaning that it is the last coat to be applied and the one seen when the coated object is examined. Lacquers are normally thermoplastic solution paints or varnishes, but the term is sometimes (confusingly) used to describe all clear woodfinishes. Enamels are normally thermosetting paints, hard, with a superficial resemblance to vitreous enamels.

Paint applied before the topcoat is called an undercoat. Some undercoats and related finishes may be briefly defined as follows:

- **Fillers** or stoppers are materials of high solid content, used to fill holes and deeper irregularities and to provide a level surface for the next coat.
- **Primers** are applied to the filled or unfilled surface, to promote adhesion, to prevent absorption of later coats by porous surfaces and to give corrosion resistance over metals. As their name implies, they prepare the base material for further paint application. Special pigments improve the anti-corrosive properties.
- **Surfacers**, or undercoats in decorative house painting, are highly pigmented materials containing large quantities of extender (see below). They are easily rubbed smooth with abrasive paper. They provide the body of the paint film, level out minor irregularities in the substrate and must stick well to primer and topcoat.
- **Primer-surfacers** are surfacers that can be applied direct to the object’s surface (the substrate), and fulfil both of the functions above in one coat.
- **Sealers** are clear or pigmented materials applied in thin coats to prevent the passage of substances from one coat of paint to another or from the substrate into later coats. They can be required to improve adhesion between coats, where this is otherwise weak.

All these materials are formulated on the principles described above. These are illustrated in Fig. 7.1, which also lists some of the minor ingredients of a paint. Some of the terms in the diagram need a little further explanation at this stage:
Fig. 7.1 Components of paints.

- **Pigment.** Any fine solid particles that do not dissolve in the varnish. If they do not provide colour they are called **extender** particles. Extenders are much cheaper than prime pigments and can carry out many useful functions, e.g. improvement of adhesion, ease of sanding and film strength.

- **Film-former.** When the coating is dry the film-former is a polymer, but in the wet sample it may be the chemical ingredients, only partly polymeric, which react to form the final dry polymer.

- **Liquid.** Some of the liquids of the paint are often withheld from the paint container and supplied separately as a **thinner.** Users add thinner to adjust the consistency to their requirements.

- **Additives.** Small quantities of substances added to carry out special jobs, such as the improvement of surface appearance.

**Application**

These are the basic ingredients, but much care in formulation will be required to produce a paint that will be easy to apply under changing conditions and pleasant to look at when dry. It is not within the aims of this book to discuss the methods of application that are available. They are well described elsewhere (see Appendix A). Suffice it to say that the paint may be put on by brushing, by roller, by a whole variety of methods of spraying (compressed air, airless, electrostatic and aerosol spraying), by dipping, electrodeposition, curtain-coating and flow-coating. Either the article is immersed in the paint, the excess of which is then allowed to drain off, or the correct quantity of paint is applied to the article and must not drain, ‘run’ or ‘sag’.

In all cases, any irregularities in the wet film caused by the method of application must flow out to leave a smooth surface.
The first problem is to make the paint easy to handle while it is being applied. Different application methods require paints of different consistency, but in all cases the principle is the same: the greater the content of dissolved polymer in a paint, the more viscous it will be. The weight percentage of involatile material found in the paint is known as the solids content or ‘solids’ of the paint. Either by adjusting the ‘solids’ of the paint, or by altering the balance of the types of liquid used, the formulator brings the consistency or viscosity of the paint to that required.

So far so good. The difficulty lies in the next stage. Most methods of application leave some irregularities in the wet film surface: brush marks, spray mottle, roller stipple and so on. These are the methods that apply the correct amount of paint, which must flow at first to remove the irregularities, and then stop flowing, to prevent ‘running’ or ‘sagging’ of paint on vertical surfaces. This change in the rate of flow is usually brought about by evaporation of solvent, causing a rise in ‘solids’ and hence a thickening of the consistency. Flow dwindles until it is scarcely occurring at all. Then the drying mechanism takes over to set the film. A very careful balance of solvents is required to do this satisfactorily and more will be said about this in Chapter 9.

An alternative method, often used in conjunction with solvent evaporation, is to include some material in the paint which gives it abnormal viscosity characteristics, so that it is fluid while being agitated, but thickens up over a period when the agitation stops. This type of paint is said to be ‘thixotropic’. More detail is given in Chapter 10.

If the article is allowed to drain after being coated, as in dipping, then it must drain evenly and not so rapidly that the film thickness becomes too low. If possible, thicknesses at the top and bottom of the article must vary only slightly, in spite of the downward drain of paint. Again the same principles must be used to slacken the flow.

With spray application in particular, the position is further complicated by the fact that the paint reaching the surface does not have the same composition as that leaving the spray-gun. The paint is broken up into thousands of fine droplets as it leaves the gun, each droplet presenting a surface – at which evaporation occurs – that is large compared with the droplet’s volume. A great deal of liquid can be lost and this must be taken into account in formulating the paint.

It is necessary to point out that this loss of solvent – all of which has been paid for – is only accepted by the paint users on sufferance, as an inevitable consequence of the process. They are constantly looking for new materials which will contain less wasted material: in other words they want paints with higher ‘solids’. Increasingly thinners other than water are all seen as hazardous to some degree and undesirable; also legislation is being enacted to reduce the amount of organic material which can be exhausted into the atmosphere, thereby polluting it. Furthermore, solvents come from petroleum, the world stocks of which are limited and must be conserved. For all
these reasons, the paint formulator chooses the ingredients to give the highest 'solids' possible.

To keep the paint manageable at high solids, the formulator has to keep the polymer molecular weight down since, as will be seen in Chapter 9, this reduces the viscosity. Alternatively (Chapter 9 again), it is necessary to take the polymer out of solution (if this is practicable and suitable) and make a dispersion or 'emulsion' paint.

Dry film properties

An outline paint formula has been described and it has been shown that application presents problems which influence the formula. After application comes drying, but before this is considered, the properties required from the dry film must be discussed, since these influence the choice of method of drying.

If the dry paint film is to be a useful one, it must stick to the surface beneath, be hard enough and flexible enough for the purpose for which it is used and must retain most of its protective and decorative properties for a long period. The paint should be capable of repair or renovation. Let us now take these requirements separately and see how they are achieved.

Adhesion

We have seen that most molecules or atoms have some attraction for one another. The strength of this attraction varies greatly with the atoms concerned, but all intermolecular attractions have one thing in common: they operate over comparatively short distances (<10 nm) and become weaker the farther apart the atoms are within that short range. At distances above 1 nm their contribution to adhesion is negligible.

Since these attractive forces are the ones that make things stick together, the first problem is to get the molecules within range, i.e. the paint film must 'wet' the surface, displacing air and all the other adsorbed materials. The critical surface tension ($\gamma$) of a smooth solid surface is a numerical measure of the ease of difficulty of wetting it. It is equal to the highest surface tension possessed by any liquid that will spread spontaneously when placed on it. If a paint is to wet the surface, it must have a surface tension equal to or lower than the critical surface tension of the solid. Plastics can have very low critical surface tensions (e.g. polytetrafluoroethylene, PTFE = 18.5 nN m$^{-1}$; polyethylene = 31 nN m$^{-1}$), which limit considerably the choice of solvents for paints to be applied to them (methods of overcoming this are disclosed in Chapter 17).

Clean metals generally have higher critical surface tensions (>73 nN m$^{-1}$), but even the thinnest possible layer of adsorbed oil or grease can dominate the surface (e.g. $\gamma$ for 'clean' tinplate cans has been measured as 31 nN m$^{-1}$), leading to wetting problems. Even if the paint wets the contaminated surface, loosely adhering grease, dirt or rust is a menace since,
although the paint may stick well to the adsorbed layer, the latter can easily come away from the surface taking the paint film with it. For this reason the cleaning of surfaces before painting is always recommended. The practice of rubbing undercoats with abrasive paper not only provides a level surface for the next coat but also cleans the surface, removing materials difficult to wet or poor in cohesion.

Semi-porous undercoats or surfaces can offer good adhesion by a different mechanism. Providing the liquid paint can displace air from the crevices, the change from liquid to solid will mechanically lock or ‘key’ the paint on to the surface (Fig. 7.2). If the clean surface is not porous, but has been wetted well, adhesion will depend on the strength of the paint–substrate intermolecular attractions. Sometimes these can be considerably enhanced by the inclusion of particular chemical groups in the molecules of the paint film-former, e.g. carboxyl groups promote adhesion to metals.

**Hardness, toughness and durability**

These properties are connected in that cross-linked films are generally harder, tougher and more durable than those that are not. High molecular weight linear polymers, however, produce harder, tougher, more durable films than their low molecular weight equivalents. If the molecular weight is high enough, a polymer can be as hard, as tough and as durable in linear form as it can be in cross-linked form.

**Flexibility**

Hardness often goes with brittleness, and brittle films – particularly those subjected to temperature changes – do not survive long, failing by cracking and then flaking off if adhesion is only mediocre. Flexibility is introduced into cross-linked films by spacing out the cross-links, so that the whole structure becomes a looser, more open cagework of molecules.
Linear polymers are made more flexible by admixture with smaller molecules, which separate the large polymer chains, reduce attractive forces between them and act as a lubricant, allowing the polymer molecules to slide past one another more easily. These smaller molecules are called plasticizers.

Some monomers give more flexible polymers than others. They may be copolymerized into brittle polymers to increase flexibility.

**Loss of decorative properties due to weathering**

Gloss may diminish, the surface ultimately becoming powdery, or the colour may fade or darken. Ultraviolet rays and water, as well as oxygen in the air, gradually attack paint films, breaking chemical bonds and causing polymer molecules to break up into smaller fragments. The surface gradually wears away, roughens and the gloss disappears. Polishing will often rub it smooth again. This type of wear is reduced by choosing resistant polymers and by keeping the proportion of pigments down. If the pigment volume concentration in the film is high, it will only require the breakdown of a small amount of polymer to cause the detachment of surface pigment particles. The powdery surface is said to have ‘chalked’.

Colour fastness is dependent on the use of high quality pigments, though complete satisfaction is not guaranteed unless the pigments have been tested with the binder that is to be used in the proposed paint.

**Ease of repair and surface renovation; solvent resistance**

Paint users often need to be able to make good damage to paint films. The ‘damage’ may be no more than excessive dirt or dust pick-up during application, spoiling the appearance. It might be shallow scratching. In either case, all that may be needed is light abrasion followed by polishing. To polish well, a surface should be capable of being softened by the heat generated, so that it will partially flow, evening out irregularities. If the polymer is cross-linked, its rigid network of chains of atoms restricts this softening and flow. The best polishing properties are usually shown by linear polymers. Their ability to reflow was demonstrated in the acrylic lacquer process used for cars, in which the lacquer surface was rubbed with very fine emery paper to remove dust and spray mottle. Subjecting the lacquer to heat in an oven reflowed the scratches, so that the surface was bright and glossy again.

Linear polymers also remain soluble in solvents: cross-linked polymers are not soluble. Thus the surface of a linear polymer film can be levelled by light rubbing with a pad soaked in a solvent mixture that will just dissolve the polymer. This process is called ‘pulling over’ and is used in the furniture industry.

If the paint film is badly damaged, it must be patched. A linear polymer film can be patched by spraying in the damaged area with the same paint.
The solvents redissolve the edges of the existing film, marrying the new area into the old. Cross-linked polymer films will not redissolve and so will not patch in this way. The complete area must be rubbed down and repainted. Any attempted patch will be at best partially successful, with all sorts of trouble likely to occur at the join between the patch and original film.

In property terms, it follows that linear polymer films will have poor resistance to solvents (present in many household articles, e.g. nail varnish). Cross-linked films will be more resistant.

If a paint is to be formulated for a particular purpose, the properties required from the dry film are defined first. These properties and the desired minimum solids of the paint may well determine whether the dry film is to contain a linear or a cross-linked polymer. When the type of polymer film has been selected, the choice of drying mechanism will have been restricted to a narrower area.

**Dry paint: how paints dry**

In the can of paint the mixture of substances must remain stable for long periods, so the ingredients must not react with one another chemically. Yet the paint must dry on the coated surface. Under some conditions some paints do not dry, which shows that the drying process does not merely consist of evaporation of the liquid. In fact there are three broad mechanisms of drying, two of which involve further chemical reaction.

**Drying without chemical reaction**

In this case the paint does dry solely by evaporation of liquids. The polymer is already fully formed in the can and, when free of solvent, is relatively hard and not sticky. During the drying process there is no chemical change in the polymer. If it was dissolved in the liquid solvents of the paint, it remains soluble in those solvents. If it was carried as an emulsion or colloid dispersion, it is not soluble in the liquid carrier, but it will be soluble in other solvents because it is a linear polymer. More is said about the sintering of particles of linear polymer into a continuous film in Chapter 11.

Nitrocellulose lacquers and decorative emulsion paints dry by this process. It is sometimes called 'lacquer drying'.

**Drying by chemical reaction**

There are undoubtedly advantages in producing a dry paint film containing cross-linked polymer as the film-former. Such polymers are, however, insoluble and so cannot be dissolved in solvents to form the vehicle of the paint in the can. We are therefore forced to have linear (or lightly branched) polymers, or even simple chemicals, in the can and to carry out a cross-linking
chemical reaction after the paint has been applied. This can be achieved in two principal ways.

Drying by chemical reaction between paint and something outside the paint

Oxygen and water vapour in particular are reactive chemical ingredients of the air. In Chapters 12 and 16 it will be shown how oxygen reacts with drying oils and other unsaturated compounds to produce free radicals and bring about chain growth polymerization. In Chapter 15 we will see how the reaction between water and isocyanates can cause step growth polymerization. Both reactions can give a cross-linked film. In both cases the principle is the same: the air is used as a chemical reactant and is kept apart from the reactive ingredients in the paint by the tightly fitting lid on the can. Assuming that the air is completely excluded, no reaction begins until the paint film is applied, presenting a large surface exposed to the air. As the solvents evaporate, cross-linking begins and the soft, sticky, low molecular weight, linear or branched polymers in the paint are converted to a hard, tough, cross-linked film which will no longer dissolve in the solvents used in the original paint or in any others.

However, if the can lid is not tight fitting, it may cause the formation of a skin, which seals off the paint below from further reaction with the air. Alternatively, the skin may be permeable to the air and the reaction may spread right through the paint, turning it into a cross-linked polymer swollen with solvent. This is called an irreversible gel and, of course, at this point the paint becomes useless.

The drying process is relatively slow at room temperature, chiefly because the reactive ingredients in the air must penetrate into the film before full hardening can occur. The paint hardens more rapidly if the reactive molecules in the paint are large. The effect of cross-linking is to build bigger and bigger molecules. Eventually the whole film could become one molecule. If the building ‘bricks’ (the original molecules) are large, less ‘cement’ (cross-links) will be needed to join them together and the whole job (the hardening) will be done faster. However, as we have seen, there are advantages in keeping the molecular size down from the point of view of application and economy. As a compromise, low molecular weight polymer (molecular weight 1000–5000) or large simple molecules are generally used. This leads to moderately high solids in the paint, decidedly a point in favour of cross-linking systems.

Chemical reaction with the air can continue long after the paint film is apparently dry to touch and, in fact, the paint film will change its chemical nature slowly all the time it is in use. This means that the properties of the paint film also change gradually. Glossy house paints derived from drying oils dry by reaction with the air.
The principle of keeping the paint stable by having one reactant outside the can is quite general. Chemicals not normally in the air can be introduced into air in a confined drying chamber. This technique is used in the ‘vapour curing’ of isocyanate paints (Chapter 15).

Alternatively, the reactive ingredient can be in the substrate before it is coated, or in a previous coating on the substrate. This principle is used in the ‘contact process’ for curing unsaturated polyester coatings (Chapter 16).

The application of these separation techniques is limited only by the chemistry of individual paint systems and the imagination of paint chemists.

Drying by chemical reaction between ingredients in the paint

Obviously the paint must remain chemically stable in storage, and the reactants must not react until the paint has been applied, yet (in this method) they must all be in the paint. This paradox is resolved either by separating the reactive ingredients in two or more containers and mixing just before use or by choosing ingredients which only react at higher temperatures or when exposed to radiation of some form. The former method produces what is known as a ‘two-pack paint’. Two-pack paints are less popular than their ready-mixed equivalents, because measuring is required before mixing and because of the limited period after mixing during which the paint remains usable (the ‘pot life’). Sometimes two packs are avoided by so diluting the reactants with solvent that reaction proceeds only very slowly in the can, but much more quickly on a surface once the solvent has gone. Here the paint is not really stable, but a tolerable ‘shelf life’ is obtained. Whichever method is used, the chemical reactants may be sticky, low molecular weight polymers, or they may be simple chemicals. The reaction produces a cross-linked polymer.

Industrial stoving enamels and anti-corrosive two-pack epoxy coatings dry by chemical reaction of their ingredients.

A summary of the properties associated with the drying mechanisms is given in Table 7.1.

Relative merits

It has been shown that paints are simple in outline, but complex in operation and formulation. How can the best choice of the many ingredients available be made? The choice of pigments and solvents is discussed in the next two chapters. This summary is concerned with the film-former.

Cross-linked or not cross-linked? There are points in favour of both alternatives. The hardest, toughest, most durable and solvent-resistant films contain cross-linked polymers, and these are applied at higher solids. If they are to be matched in all respects except solvent resistance, linear polymers of high molecular weight must be used. For solution polymers,
this inevitably means much lower solids at application viscosity. Although higher solids, without loss of molecular weight, can be obtained with emulsion systems, these have their own special formulation problems (Chapter 11).

Against this can be argued the ease of polishing, pulling over or reflowing and the good patching properties of linear polymers. It is also a much simpler, fast method of drying that is not particularly temperature sensitive and produces little or no handling or storage problem. There is no right or wrong here. It simply depends on the job the paint has to do, the drying facilities available, the requirements of the user and whether the difficulties mentioned are slight or severe with the particular resins being suitable for the job.
Pigmentation
pigments and paint making

The outline formula of a paint has been given in Chapter 7 and the nature of polymers and resins has been described in Chapter 5. In the next three chapters, the other main ingredients of surface coatings will be covered briefly, before particular paints are described in the remainder of this book.

A detailed study of the chemistry of pigments is beyond the scope of an introductory book such as this and is already available elsewhere (see Appendix A). Instead, this chapter reviews some of the key properties of pigments and discusses their selection and methods of incorporating them into paint.

Pigment properties

Any surface coating pigment will need to carry out some (or perhaps, all) of the following tasks:

- to provide colour;
- to provide special effects (e.g. flip, sparkle);
- to obliterate previous colours;
- to improve the strength of the paint film;
- to improve the adhesion of the paint film;
- to improve the durability and weathering properties;
- to increase the protection against corrosion;
- to reduce gloss;
- to modify flow and application properties.

To choose a pigment to carry out a given selection of these nine functions, we must know about the following properties of the pigment:

- tinting strength;
- lightfastness;
- bleeding characteristics;
- hiding power;
Pigmentation

- refractive index;
- particle size;
- particle shape;
- specific gravity;
- chemical reactivity;
- thermal stability.

**Tinting strength**

The majority of paints contain white pigment, which is tinted to the appropriate pastel or mid-shade with coloured pigments. If a lot of coloured pigment is required to achieve the shade, it is said to have poor tinting strength. The tinting strength of a coloured pigment is related to that of some standard pigment of similar hue. If numerical values are given, then

\[
\text{amount of alternative pigment required to produce the shade pigment} = \frac{\text{tinting strength of standard pigment}}{\text{tinting strength of alternative pigment}} \times \text{amount of standard pigment required}
\]

The tinting strength of a pigment is independent of its hiding power, since the comparison of shades is done at film thicknesses that completely hide the substrate. Relatively transparent pigments can have high tinting strengths.

The phrase ‘tinting strength’ is sometimes applied to white pigments. A single coloured pigment is used for the comparison of white pigments at a fixed shade.

**Lightfastness**

To give a good colour initially is not enough. The colour must last, preferably as long as the paint film. Many pigments fade or darken or change shade badly in the light. This is because the ultraviolet rays in sunlight are sufficiently energetic to break certain chemical bonds and thus change molecules. A change in chemical structure means a change in the ability to absorb light in the visible region of the spectrum, with a consequent loss of colour or variation of hue. On the other hand, if the pigment can absorb ultraviolet rays without breakdown, it will protect the binder. The energy is dissipated harmlessly as heat.

**Bleeding characteristics**

Not all pigments are completely insoluble in all solvents. Colour in the right place is all very well, but when white lettering applied over a red background turns pink, it is not so good.
What happens is that the solvents of the white paint dissolve some of the red pigment in the background coat and carry it into the white overlayer. Organic reds as a group are particularly prone to this fault (though theoretically it can occur with any colour), so it has been given the name ‘bleeding’.

**Hiding power**

Ideally one coat of paint should obliterate any colour. Frequently two are needed, but in any case the total thickness of paint applied should be no more than that necessary for the required degree of protection of the surface and the presentation of a smooth, pleasing appearance. Such thicknesses are surprisingly small, usually 25–100 μm. To obliterate, the pigments used must prevent light from passing through the film to the previous coloured layer and back to the eye of an observer. The pigments do this by absorbing and scattering the light. The hiding power of a paint is expressed as the number of square metres covered by 1 litre of paint to produce complete hiding; the hiding power of a pigment is expressed as the number of square metres covered per kilogram of pigment, which has been dispersed in a paint and applied so that it will just hide any previous colour.

Hiding power depends upon the wavelengths and total amount of light that a pigment will absorb, on its refractive index and also on particle size and shape.

**Refractive index**

Chapter 6 showed how light rays can be bent and how they may be returned to the eye from a paint film. The light rays suffer refraction, diffraction and reflection by transparent particles that have a refractive index differing from that of the film in which they lie. White pigments are transparent in large lumps, but white in powder form, because they have high refractive indices (2.0–2.7). These are greater than the refractive indices of film-formers (1.4–1.6), so the pigments give a film its white colour by the mechanism described for incompatible resins in Chapter 6. Titanium dioxide (TiO₂) pigments, in particular, have excellent hiding power, because their refractive indices are so much higher than those of film-formers and because they have the optimum particle size. Extender pigments are also transparent in bulk and white as powders, but they do not colour paints because their refractive indices scarcely differ from those of film-formers.

**Particle size**

There is an ideal particle diameter for maximum scattering of light at interfaces and this is approximately equal to the wavelength of the light in
the particle. As a rough guide, the optimum diameter is approximately half the wavelength of the light in air, i.e. about 0.2–0.4 \( \mu \text{m} \). Below this size the particle loses scattering power; above it, the number of interfaces in a given weight of pigment decreases. The hiding power of the transparent pigment is reduced. Pigments have particle diameters varying from 0.01 \( \mu \text{m} \) (carbon blacks) to approximately 50 \( \mu \text{m} \) (some extenders). No sample of pigment contains particles all of an identical size; rather there is a mixture of sizes with an average diameter.

Connected with particle size are surface area and oil absorption. If a cube of pigment is cut in two, the weight of pigment is the same, the number of particles is doubled, the size of particle is halved and two new surfaces are formed along the cut, in addition to all the original surface of the cube. Thus in any fixed weight of pigment, the smaller the particles, the larger the area of pigment surface.

It is interesting to note that while 1 gram of rutile titanium dioxide white (particle diameter 0.2–0.3 \( \mu \text{m} \)) has a surface area of 12 m\(^2\), 1 gram of fine silica (particle diameter 0.015–0.2 \( \mu \text{m} \)) has a surface area of 190 m\(^2\) – about the area of a singles court at tennis!

The surface area is indicated by the oil absorption, which is the minimum weight in grams of a specified raw linseed oil that is required to turn 100 g of pigment into a paste. The oil is added slowly to the pigment with thorough mixing and shearing between the walls of the vessel and a rod. While the oil is in the process of replacing air molecules on the particle surfaces (this is called wetting the pigment), the pigment–oil mixture remains a crumbly mass. Pigment, as Fig. 8.1 shows, in the dried powder is in the form of agglomerates, with particles packed together, but with air between the individual particles. These need breaking down in dispersion processes and the prime pigment particles separating.

When wetting is as complete as it can be, the next additions of oil will fill the spaces between the particles. As soon as there is a slight oil surplus, the mixture becomes a paste, because the particles are free to flow past one another as a result of the lubricating action of the oil. It can be seen that,

![Fig. 8.1 The pigment dispersion process.](image)
while the oil absorption value is related to the surface area, it depends on how successful the operator is in displacing all the air from the whole surface.

With many pigments the operator will not be at all successful, using such rudimentary equipment. Some surfaces will have more attraction for linseed oil molecules than others. Obviously the greater the area of pigment left unwetted, the lower the oil absorption will appear to be. If the volume of space between the particles varies, as it will do from pigment to pigment according to the particle shape and distribution of sizes, then this will also affect the final figure. At best, oil absorption is a rough guide to surface area, but its merit is that it is easily and quickly measured and gives the paint formulator some idea of the type of pigment that is being dealt with.

The most important part of a pigment particle is its surface. At the surface are those chemical groups that will make contact with the chemical groups in the varnish. These surface groups will determine whether the pigment has any attraction for varnish molecules or not (whether the pigment is easily wetted) and whether the pigment has special attractions for parts of the varnish (e.g. drier molecules, see Chapter 12). This latter feature may be undesirable, since molecules firmly attached to pigment surfaces are not free to move about and carry out their functions in the varnish. If they are molecules of a paint additive, they are bound to be present in small quantities; a pigment of very large surface area could totally absorb the additive, rendering it ineffective. If these groups on the pigment surface attract each other strongly, the pigment particles will tend to cluster, resisting wetting and dispersion and setting up a loosely bound 'structure' of particles in the paint, which will affect its application properties (see Chapter 10). This phenomenon is called flocculation. If the chemical nature of the pigment surface is not known, it is a general rule that the larger the surface area, the more active the pigment surface will appear to be.

**Particle shape**

Particles may be nearly spherical, cubic, nodular (a rounded irregular shape), acicular (needle- or rod-like) or lamellar (plate-like). Since particle shape affects pigment packing, it therefore affects hiding power. Rod-shaped particles can reinforce paint films, like iron bars in concrete, or they may tend to poke through the surface reducing gloss.

Such rough surfaces may help the next coat to stick more easily, so this type of pigment could be useful in an undercoat. Plate-shaped particles tend to overlap one another like tiles on a roof, making it more difficult for water to penetrate the film. Aluminium and mica pigments have this shape. Thus more protection is given with micaceous iron oxide-containing paints, and by heat-resistant aluminium paints. Aluminium and specially treated mica pigments also reflect light from their polished flat faces in metallic paints.
formulator is very much in the hands of the pigment manufacturers and must rely on their literature.

**Thermal stability**

The temperature at which a pigment decomposes or alters its nature (e.g. melts) can be very important if the pigment is required for a paint to be stoved at high temperatures, or if the paint is to be heat resistant.

Where is all this information to be obtained? Partly in general pigment and paint literature (where traditional pigments and well-defined groups of pigments are concerned), partly from the technical literature supplied by the pigment manufacturer and partly by experiment. For a reference to experimental methods for determining pigment properties, see Appendix A.

**Pigment types**

Whole books have been written on pigments classified by chemical types. Here we have room only to attempt a much broader classification and to say a few words about the implications of the classification. All pigments are either:

- natural or synthetic; and
- organic or inorganic chemicals.

**Natural and synthetic pigments**

It is unlikely that there is any organic pigment, the naturally occurring form of which is still in industrial use today. Many inorganic pigments, however, are still dug out of the earth’s crust, crushed, washed and graded by size. Frequently, there is a synthetic equivalent – i.e. a pigment made from other ingredients by a chemical process – apparently the same chemically, but often different in properties. The differences arise because:

- whereas the natural pigment is available in the crystal form found in nature, the synthetic product may be induced to take a more desirable crystal shape;
- the natural product may be contaminated by some impurity, such as silica, which it is uneconomic to remove; the synthetic product should be pure or nearly so;
- crushing produces a wide range of particles sizes and grading methods may not be able to remove all oversize or undersize particles from desired range; a pigment produced by precipitation under controlled conditions should have a much more uniform size range.
The chief family of pigments in which natural varieties are still of importance is the iron oxide family: ochres, umbers and siennas; red, yellow and black iron oxides.

**Organic and inorganic pigments**

There are now far more organic pigments than inorganic ones, though some of the newest contain both metallic (inorganic) elements and organic structures. Again, many organic pigments are organic chemicals deposited on an inorganic (e.g. aluminium hydroxide) ‘core’. These pigments are called **lakes**. It is difficult to lay down hard and fast rules, as there are exceptions in every case, but for some properties there is a clear-cut advantage for the bulk of one type of pigment over the majority of the other type. These properties are listed in Table 8.1. This list may give the impression that it is best to avoid organic pigments, but their brilliance and clarity are very powerful arguments for using them. The very best organic or organometallic pigments give the highest standard of performance for most uses, e.g. the

<table>
<thead>
<tr>
<th>Table 8.1 Properties of pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>Brilliance and clarity of hue</td>
</tr>
<tr>
<td>White and black paints</td>
</tr>
<tr>
<td>Non-bleeding</td>
</tr>
<tr>
<td>Lightfastness</td>
</tr>
<tr>
<td>Heat stability</td>
</tr>
<tr>
<td>Anti-corrosive action</td>
</tr>
<tr>
<td>UV absorption</td>
</tr>
<tr>
<td>Reflective effects</td>
</tr>
</tbody>
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phthalocyanine ('Monastral') pigments, the quinacridone ('Cinquasia') pigments, the perylene and perinone pigments, the dioxadine pigments and the high molecular weight azo pigments.

**Pigment selection**

To sum up, the paint formulator's method of pigment selection is as follows.

- Examine a pattern of the colour to be produced in paint. Estimate the number of different hues that will have to be blended to produce the colour. A suitable pigment has to be found to provide each hue.
- Define the properties required from the pigments.
- Select a suitable pigment or pigments in each hue. In order to obtain pigments with the required properties, consult the following sources where necessary:
  - General paint and pigment literature. There are traditional pigments for particular uses and binders.
  - *The Colour Index* (Society of Dyers and Colourists, Bradford, UK). The properties of pigments are given, together with the names of commercial grades and their manufacturers.
  - Pigment manufacturers' literature. Examples of colour may be given.
- Match the colour (see below) with one or more pigment combinations.
- Test the paints produced.

**Dispersion**

The next stage is to get the pigment into the paint. The pigment is usually supplied as a powder, in which the granules are actually aggregates of the fine particles produced by the pigment manufacturer. These particles must be dispersed or separated from one another and evenly distributed throughout the paint as a colloidal suspension. For this suspension to have the maximum stability in organic solvents, the surface of each particle should be completely wetted with the varnish; there should be no intervening layers of air or adsorbed water.

Wetting with solvent alone is not enough and pigment dispersions in solvent have poor stability. Each particle in the pigment suspension must be stabilized by polymer chains, anchored to its surface by intermolecular attractions, yet extending out into the varnish because of their attractions for the solvent molecules. When two such particles approach one another, they do not adhere. Contact between them involves the intermingling of polymer chains from the two particles. Locally, in the region between the particles, the concentration of resin molecules is higher than at other points in the paint. This upsets the equilibrium of the system, so solvent molecules diffuse into this region, dilute the concentration and restore
equilibrium. The osmotic pressure involved is sufficient to separate the particles.

A resin suitable for dispersion usually contains polar groups (which provide the attraction for pigment surface molecules) and is completely soluble in the solvent mixture of the dispersion. Sometimes, surfactants (Chapter 10) are used to bridge the particle–resin interface and assist wetting. In water, ionic surfactants (e.g. soaps) can provide the pigment surface with an electrical charge. The particles, being of like charge, repel one another and the dispersion is stable.

Dispersion is usually carried out in a mill, a machine in which the agglomerates are subjected to the forces of shear and (sometimes) attrition. When shear is the dispersing action, the agglomerates are squeezed between two surfaces moving in opposite directions, or in the same direction but at different speeds. It is just like making cocoa, where the powder has to be dispersed in a little milk to form a paste. Dispersion is carried out by a shearing motion between spoon and cup. In paint mills the principle is the same, but the power and degree of dispersion are much greater.

During the manufacture of the pigment, the particles are reduced to their ultimate size by crushing or grinding in a liquid slurry, where impaction forces are used in a process known as comminution. Where attrition or rubbing forces are part of a dispersion process, the conditions are much milder and there is no attempt to fracture individual particles. In the viscous medium of the varnish, agglomerates – not particles – are broken down.

Several types of mills are used, depending on the difficulty experienced in dispersing the particular pigment. The high speed disperser (Fig. 8.2) is used
for easily dispersed pigments and consists of a horizontal disc with a serrated edge (Fig. 8.3), which rotates are high speed about a vertical axis. The dispersion quality may not however be sufficient for full gloss paints. However, pre-dispersion in a high speed disperser may be the preliminary to faster throughput to a sand or bead mill.

The **ball mill** is a cylinder revolving about its axis, the axis being horizontal and the cylinder partly filled with steel or steatite (porcelain) balls, or pebbles. The speed of rotation is such that the balls continually rise with the motion and then cascade down again, crushing and shearing the pigment. Depending on the method of loading, the ball mill can provide actual grinding or size reduction by impaction. This is rarely required, but its ability to provide extreme conditions means that it can be used for the most difficult pigments, such as carbon black. Since grinding times are long, for economic reasons ball mills are only used for these pigments.

In the **sand mill** (Fig. 8.4) or **bead mill**, the axis of rotation may be horizontal or vertical, the grinding medium is coarse sand or beads (glass, zirconia) and the charge is induced to rotate at higher speeds by revolving discs in a stationary container. The ball mill produces a batch of pigment dispersion; the sand grinder gives a continuous output of dispersed pigment. Sand or bead mills in a variety of configurations are now the most frequently used dispersing machinery.

**Roller mills**, which have their major use in ink production, consist of a number of horizontal steel rolls placed side-by-side and moving in opposite directions, often at different speeds, with very small clearances in between. In these gaps, the pigment–resin mixture is sheared. The **triple roll mill** is shown in Fig. 8.5. A paste is fed in at D, is lightly sheared between rollers A and B and more severely between B and C. A scraper blade E removes the dispersion. All rollers are independently driven and run at different speeds to increase shear. The mill is particularly suitable for the production of pastes of very high pigment content.

Several other mills are available, which the reader may discover elsewhere (Appendix A). These few examples are quoted to illustrate the principles involved.
It is obvious from the mention of stiff pastes that the whole paint is not charged initially into the mill. In fact, the paint maker aims to put in the maximum amount of pigment and the minimum amount of resin to obtain the largest possible paint yield from the mill. This mixture forms the grinding stage. When the dispersion is complete (after a period varying from 10 min to 48 h according to the materials and machinery involved), the consistency is reduced with further resin solution or solvent. This is the 'let-down' stage and may take up to 2 h. The third or final stage (carried out in a mixing tank) consists of the completion of the formula by addition of the remaining ingredients and any necessary tinting. A breakdown of a possible
The amount of pigment in the formula is that required for the appropriate colour, hiding power, gloss, consistency and durability. As a rough guide, the amount might vary from one-third of the binder weight to double the weight (for a paint, when including extender).

**Colour matching**

The colour of a paint is usually matched to some colour pattern. It must, at any rate, be matched to the colour of the previous batch of the same paint. If a new shade is to be matched in a paint, the procedure for matching is as follows.

- The main hue and the undertones are observed; also whether the colour is 'clean' or 'dirty'.
- From experience and by application of the principles of subtractive mixing, the pigments likely to give the colour are chosen. The procedure is described under Pigment selection (above).
- Each of these pigments is dispersed separately and each dispersion is converted to a paint. The colour matcher now has several paints, each containing only one pigment. These are known as *colour solutions*.
- The colour solutions are blended, the choice of solutions and proportions being varied, until finally the correct blend to give the colour is obtained. The proportions of pigment in this blend are recorded.
- The final paint is often made by blending colour solutions, but frequently a more stable dispersion is obtained if all the pigments are dispersed simultaneously in the same mill. This is called *co-grinding* the pigments. If the colour is then slightly off shade, it is adjusted by additions of colour solutions or concentrated pigment dispersions.

In larger paint companies, where spectrophotometers or colorimeters and a computer are available, these stages can often be speeded up considerably. The new shade can be measured by the colorimeter and expressed precisely as a group of numerical values. This information can be passed to the computer, which has been previously programmed with the values for numerous pigments and with the 'rules' governing the mixing of these pigments to give the desired colour. The computer will then print out a choice of pigments (type and proportions) for achieving the colour.

The formulator makes a selection and will usually find that the colour that is produced to the computer's instructions will be close to the desired colour and that the recipe will require only minor modifications to give the exact shade.

Most colours, even dark ones, require substantial proportions of white pigment. Clean colours require organic pigments and should be matched with the minimum number of pigments. The subtractive effect increases with the number of pigments, reducing the reflected light intensity and
hence ‘dirtying’ the colour. If darkening or ‘dirtying’ of a colour is required, it can be done with black pigment. The use of black pigment can markedly alter the shade. Thus brown is a mixture of yellow (or red) and black.

Paint making and mixing schemes

While the description of the paint-making process may have given the impression that all paint is essentially made as a batch process, starting from the ingredients and ending with paint, the colour matching description will have given hints that other approaches are possible. While white paints will essentially be based on titanium dioxide pigment, possibly with some extender, coloured paints invariably contain a number of pigments.

In larger factories, colour solutions may be made and stocked in large quantities, providing storage is available for the required range. This is especially applicable to making industrial paints, where this may be the only economical way to make a range of colours and batch sizes, and where a quick and flexible response to customer orders is required.

This mixing concept has been extended into two large paint markets, to give in one case extended customer choice, and in the other, the only possible means of access to the colour range required. For the decorative paint market, concentrated tinters have been developed, often capable of use in both solvent and water-borne paints, to offer the customer a wider choice of colours than is possible with a standard range, often limited by shelf storage space in the shop. The shop will be equipped with a dispenser for the tinters, and a can-shaker to ensure complete mixing.

For the car refinish market, it is essential that every colour made can be offered, and here mixing schemes use a range of colour solutions, capable of use alone, or in any blend with any other colour. These are also used to produce metallic paints, and the paint dealer or car repairer will have recipes to mix all the colours they require. However, especially in the case of metallic paints, the spray operator may need to be skilled in using solvent and clear (unpigmented) additives on occasion to achieve the desired finish.