

1

Paint composition and applications — a general introduction

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1.1 A short history of paint

Primitive men are credited with making the first paints about 25 000 years ago. They were hunters and cave dwellers and were probably inspired by the rock formations of their cave walls to outline and colour the shapes of the animals they hunted. It is possible that by creating these images they thought their power over their prey would be increased.

Chemical analysis of cave paintings discovered at Altamira (Spain) and Lascaux (France) show that the main pigments used by Palaeolithic artists were based upon iron and manganese oxides. These provide the three fundamental colours found in most cave paintings, namely black, red, and yellow, together with intermediate tints. Carbon from burnt wood, yellow iron carbonate, and chalk may also have been used. Surprisingly, there is no trace of a white pigment (the commonest pigment in use today) at Lascaux, where the natural colour of the rock was used as a pale background. However, white pigments do occur in some prehistoric paintings in Africa.

These earth pigments were ground to a fine powder in a pestle and mortar. Naturally hollowed stones are thought to have been used as mortars and bones as pestles, following the finds of such articles stained with pigments. The powdered pigments were probably mixed with water, bone marrow, animal fats, egg white, or vegetable sugars to form paints. They were applied by finger 'dabbing', or crudely made pads or brushes from hair, animal fur, or moss. Cave paintings have survived because of their sheltered positions deep in caves which were subsequently sealed off. These paints have very poor durability, the binders serving merely to make the pigments stick to the cave walls.

The Egyptians developed the art of paint-making considerably during the period circa 3000–600 BC. They developed a wider colour range of pigments which included the blues, lapis lazuli (a sodium silicate–sodium sulphide mixed crystal), and azurite (chemically similar to malachite). Red and yellow ochres (iron oxide), yellow orpiment (arsenic trisulphide), malachite green (basic copper carbonate), lamp-black,

and white pigment gypsum (calcium sulphate) all came into use during this period. The first synthetic pigment, known today as Egyptian Blue, was produced almost 5000 years ago. It was obtained by calcining lime, sodium carbonate malachite, and silica at a temperature above 830°C. The Egyptians also developed the first lake pigments. These were prepared by precipitating soluble organic dyes onto an inorganic (mineral) base and 'fixing' them chemically to form an insoluble compound. A red dye obtained from the roots of the madder plant was used in the first instance. This is no longer used other than in artists' colours ('rose madder') because it fades rapidly on exposure to sunlight, and it has been replaced by alizarin. Lake pigments still, however, represent an important group of pigments today. Red lead was used in preservative paints for timber at this time, but was more extensively used by the Romans. The resins used were almost all naturally occurring gums; waxes which were applied molten as suitable solvents were unknown. Linseed and other drying oils were known, but there is no evidence that they were used in paints.

The Greeks and Romans in the period 600BC–AD400 almost certainly appreciated that paint could preserve as well as decorate objects. Varnishes incorporating drying oils were introduced during this period. However, it was not until the thirteenth century that the protective value of drying oils began to be recognized in Europe. During the Middle Ages much painting, especially on wood, was protected by varnishing. The varnish was made by dissolving suitable resins in hot linseed, hempseed, or walnut oil, all of which tend to darken with time.

By the late eighteenth century, demands for paints of all types had increased to such an extent that it became worthwhile for people to go into business to make paint and varnishes for others to use. In 1833, J W Neil advised varnish makers always to have an assistant present during the varnish making process, for safety. 'Never do anything in a hurry or a flutter . . . a nervous or timorous person is unfit either for a maker or assistant, and the greatest number of accidents occur either through hurry, fear or drunkenness.' This admonition is indicative of the increase in scale of manufacture and the dangers of use of open-pan varnish kettles.

The industrial revolution had a major effect on the development of the paint industry. The increasing use of iron and steel for construction and engineering purposes resulted in the need for anti-corrosive primers which would delay or prevent rusting and corrosion. Lead- and zinc-based paints were developed to fulfil these needs. It is interesting to note that one of the simplest paints based upon red lead dispersed in linseed oil is still probably one of the best anti-corrosive primers for structural steel. Lead-based paints are being superseded not because better products have been produced, but because of the recognition of their toxicity and the hazards attendant upon their use.

An acceleration of the rate of scientific discovery had a growing impact on the development of paints from the eighteenth century to the present day. Prussian blue, the first artificial pigment with a known chemistry, was discovered in 1704. The use of turpentine as a paint solvent was first described in 1740. Metal driers, for speeding up the drying of vegetable oils, came into use about 1840.

The basis of formaldehyde resin chemistry was laid down between 1850 and 1890 although it was not used in paints until the twentieth century. Likewise, it was discovered in 1877 that nitrocellulose could be made safe to use as a plastic or film, by plasticizing it with camphor, but it was not until after the First World War that it was used in any significant amount in paints. The necessary impetus for this to

happen came with the mass production of the motor car. Vast quantities of nitrocellulose were manufactured for explosives during the war. At the end of the war, with the decline in the need for explosives, alternative outlets for nitrocellulose needed to be found, and the mass production of motor cars provided the necessary market. The war had accelerated the exploitation of the discoveries of chemistry and the growth of the chemical industry. New coloured pigments and dyestuffs, manufactured synthetically, became available, and in 1918 a new white pigment, titanium dioxide, which was to replace white lead completely, was introduced. Titanium dioxide improved the whiteness and 'hiding' or obliterating power of paint, but when originally introduced it contributed to more rapid breakdown of paints in which it was used because of its photoactivity. Subsequent research has overcome this problem and ensured that the modern pigmentary forms of titanium dioxide can be used in any type of composition without suffering any disadvantage of this kind.

The most recent influences on coating developments are related to environmental considerations, and the need to conform to health and safety legislation. Cost/benefit relationships have also become more important in an increasingly competitive world market and have influenced formulation practice markedly.

Subsequent chapters of this book will be largely concerned with developments that have taken place in the twentieth century, of which most have occurred within the last fifty years.

1.2 Paint or surface coating?

The terms 'paint' and 'surface coating' are often used interchangeably. Surface coating is the more general description of any material that may be applied as a thin continuous layer to a surface. Purists regard the term 'surface coating' as tautological. However, it has been used widely in the UK and in North America to distinguish painting from other forms of surface treatment, such as electroplating, anodizing, and the lamination of polymer film onto a surface. Paint was traditionally used to describe pigmented materials as distinct from clear films which are more properly called lacquers or varnishes. We shall be most concerned with paint in the context of this book; but, as we shall see, modern painting processes may include composite systems in which a total paint system comprises several thin films, some, but not all, of which may be pigmented. We shall use both terms as appropriate to the context in which specific paint compositions are being discussed.

The purpose of paints and surface coatings is two-fold. They may be required to provide the solution to aesthetic or protective problems, or both. For example, in painting the motor car the paint will be expected to enhance the appearance of the car body in terms of colour and gloss, and if the body is fabricated out of mild steel it will be required to give protection against corrosion. If the body is formed from glass fibre reinforced plastic the paint will only be required for aesthetic purposes. There are obviously very sound economic reasons why it is attractive to colour only the outer surface of articles that might otherwise be self-coloured by using materials of fabrication, e.g. plastics that are pigmented, particularly if a wide choice of coloured effects is required. This topic will be developed in the chapters on paints for specific markets (Chapters 9–13).

In considering the nature of paints it will become abundantly clear that the rela-

tionship between the coating and the substrate is extremely important. The requirements for a paint that is to be applied to wood are different from those of a paint to be applied to a metal substrate. Moreover, the method by which the paint is applied and cured (or dried) is likely to be very different. In formulating a paint for a particular purpose it will be essential for the formulator to know the use to which the painted article is to be put, and physical or mechanical requirements are likely to be called for. He will also have to know how it is to be applied and cured. Thus, a paint for an item made from cast iron may call for good resistance to damage by impact (e.g. chipping), whilst a coating on a beer can will call for a high degree of flexibility. These different requirements will be described in Chapters 9–13 which will deal with specific areas of paint usage.

It has long been recognized that it is difficult, if not impossible, to meet the requirements of many painting processes by the use of a single coat of paint. If one lists the requirements of a typical paint system it is easy to see why. Many, if not all, of the following are likely to be required: opacity (obliteration); colour; sheen (gloss); smoothness (or texture); adhesion to substrate; specific mechanical or physical properties; chemical resistance; corrosion protection; and the all-embracing term 'durability'. Durability is an important area that we shall return to in many contexts. The number of different layers that comprise the paint system will depend on the type of substrate and in what context the coated object is used. A typical architectural (gloss) paint system might consist of a 'primer', an 'undercoat', and a 'topcoat'. All three are likely to be pigmented compositions, and it is probable that there will be more than one coat (or layer) of each of these paints. An architect may well specify one coat of primer, two coats of undercoat, and two coats of topcoat. The purpose of these individual layers and hence their composition is likely to be very different. The primer is designed largely to seal the substrate and provide a means of achieving good adhesion between substrate and undercoat. It may contribute to opacity, but this will not be its main purpose. The undercoat will be used for two purposes: to contribute significantly to the obliteration of the substrate and to provide a smooth surface upon which to apply the topcoat. The smooth surface is obtained by abrading the dried undercoat (after each coat has dried) with fine tungsten carbide paper. The topcoat is then applied to complete the process of obliteration and to provide the appropriate aesthetic effect (i.e. colour and sheen). The system as a whole would be required to give protection to the wood or metal substrate to which it is applied.

The interrelationship between these multilayers is worth considering. The mechanical and physical properties of the individual coatings will often be very different. The function of the primer in promoting adhesion has already been mentioned. It may also be required to relieve stresses that are built up within the coating system as a result of hardening and ultimately embrittlement of the topcoat (and undercoat) as a result of ageing, or to accommodate stresses imposed by the differential movement of the substrate. The softwoods used in the construction of window frames are known to expand and contract between the dry (summer) and wet (winter) conditions by at least 10% across the grain, but much smaller changes are observed in the direction of the grain. The undercoat will be formulated in a colour close to that of the topcoat, but it may serve this purpose to several closely related topcoat colours. It will normally be highly pigmented, in contrast to the topcoat which will not. The reason for the latter is the need, for example, to maximize gloss and extensibility. The use of the type and concentration of pigmentary

material in the undercoat would not be conducive to maximizing these properties in the topcoat.

The primer will frequently be required to contribute to corrosion protection. Those formulated for use on steel are likely therefore to incorporate a chemically active anti-corrosive pigment. Corrosion protection may be achieved by yet another means, the chemical treatment of the substrate. Thus many industrial coating processes involve a chemical pretreatment of metal, mainly aluminium or ferrous substrates. The latter is most frequently treated with a phosphate solution that produces a crystalline phosphate layer. Subsequent paint application, i.e. priming, is therefore to a crystalline inorganic layer and not directly to an (uncoated) pure metal surface.

Surfaces are seldom what they seem. With the exception of the noble metals almost all surfaces that will be commonly regarded as 'metal' surfaces will present to the paint a surface that is not a metal but an oxide layer. Even so the purity or cleanliness of the surface may well be an unknown quantity. Since this surface will have an important effect on such properties as the adhesive performance of the paint system it is important to appreciate this point. Just as most surfaces will be 'dirty' and thus be ill-defined, it is necessary to produce paint systems that can accommodate the contamination and general variability of surfaces. These types of system must be 'tolerant' to all but excessive contamination and are often described as 'robust' if the required degree of tolerance can be achieved. This is not to say that industrial coating processes do not require certain pretreatments such as degreasing, and may involve the chemical pretreatments indicated above.

The deterioration of paints which occurs in many situations is largely due to changes in the chemical nature of the film former with consequent changes in its mechanical properties, and research continues unabated to formulate polymers and resins to improve the performance of paints in use. The development of new improved pigments may contribute to improvements in durability, but in most cases the weakest link in the system is the film former. One consequence of this is the development of systems for specific end uses. Such approaches are adopted when it is practicable to avoid the compromises that are otherwise likely to be required for a general-purpose product. For economic and marketing reasons the best product may not be available for a specific end use, and a compromise of cost and performance may be required. Indeed the cost-effectiveness of a particular coating composition will usually dominate other considerations particularly in the industrial paint markets.

1.3 The components of paint

The composition of a paint is indicated in Table 1.1 which also indicates the function of the main components.

Not all paints have every ingredient, as will be indicated in subsequent specialist chapters. For example gloss paints will not contain extenders which are coarse particle inorganic materials. These are used in matt paints such as the surfacers or primer surfacers used in the motor industry.

Major differences occur between the polymers or resins that are used in paints formulated for different purposes. This is because of differences between the methods of application and cure, the nature of the substrate, and the conditions of

Table 1.1 — The composition of paints

	Components	Typical function
Vehicle (continuous phase)	Polymer or resin (Binder)	Provides the basis of continuous film, sealing or otherwise protecting the surface to which the paint is applied. Varies in chemical composition according to the end use.
	Solvent or diluent	The means by which the paint may be applied. Avoided in a small number of compositions such as powder coatings and 100% polymerizable systems.
Pigment (discontinuous phase)	Additives	Minor components, wide in variety and effect, e.g. catalysts, driers, flow agents.
	Primary pigment (fine particle organic or inorganic)	Provides opacity, colour, and other optical or visual effects. Is thus most frequently used for aesthetic reasons. In primers the pigment may be included for anti-corrosive properties.
	Extender (coarse particle inorganic matter)	Used for a wide range of purposes including opacity/obliteration (as an adjunct to primary pigment); to facilitate sanding, e.g. in primer surfacers.

use. Thus architectural ('decorative' or 'household') paints will be required to be applied *in situ* at ambient temperatures (which may be between 7 and 30°C depending on climate and geographical location). They will 'dry' or 'cure' by one of two mechanisms: (i) atmospheric oxidation or (ii) the evaporation of diluent (water) accompanied by the coalescence of latex particles comprising the binder. Many industrial finishing processes will require the use of heat or other forms of radiation (UV, IR, electron beam) to induce chemical reactions, such as free radical or condensation polymerization, to convert liquid polymers to highly crosslinked solids. The most common of these processing methods uses 'thermosetting' polymers which will frequently be admixtures of two quite different chemical types of material, e.g. alkyd combined with amino resin. There is a similarity between both the oxidative drying and industrial thermosetting processes in so far that in both cases the polymers used are initially of low molecular weight and the curing process leads to crosslinking of these polymers to yield highly complex extremely high molecular weight products. In contrast, it is possible to produce coatings without the need for crosslinking, for use in both of these distinctive markets. In the case of decorative or architectural paints this is exemplified by the emulsion paint, in which the binder is in the form of high molecular weight polymer particles suspended in an aqueous medium. Lacquers used in the motor industry may be based upon high molecular weight polymer in solution. Both systems avoid the need for crosslinking to achieve satisfactory film properties, but recent technological developments suggest that improved film properties can be achieved by the introduction of crosslinking in some form, e.g. by the use of microgels.

1.3.1 Polymer or resin film formers

The organic chemistry of film formers is described in detail in Chapter 2. It will be useful, however, to indicate here some of the range of polymers and resins that have

Table 1.2

Low molecular weight	High molecular weight
Oleoresinous binders	Nitrocellulose
Alkyds	Solution vinyls
Polyurethanes	Solution acrylics
Urethane oils	Non-aqueous dispersion polymers (NADs)
Amino resins	Polyvinyl acetate (PVA) } latexes
Phenolic resins	Acrylic
Epoxide resins	Styrene/butadiene
Unsaturated polyesters	
Chlorinated rubber	

come to be used as film formers, and to indicate their general areas of application. Film formers or binders may be classified according to their molecular weight. Thus low molecular weight polymers that will not form solid films normally without further chemical reaction form one class. High molecular weight polymers that will form useful films without further chemical reaction form the second class. Examples of polymers and resins classified by this means are shown in Table 1.2.

1.3.1.1 Low molecular weight film formers

Oleoresinous binders

These are prepared by heating vegetable oils with naturally occurring resins such as wood rosin, fossil resins such as Congo Copal and Kauri gum. They would also include oil-modified phenolics. To a large extent these types of resinous binder have been displaced by alkyd resins and the like, but many are capable of providing products that in performance are the equal of their successors, particularly in specific applications such as in architectural undercoat paint. They are less reproducible than condensation polymers like alkyds and are less attractive in terms of modern manufacturing processes.

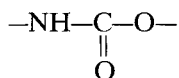
Alkyds

Alkyds are polyesters derived as the reaction products of vegetable oil triglycerides, polyols (e.g. glycerol), and dibasic acids or their anhydrides (e.g. phthalic anhydride). They are generally formulated with very different end uses in mind, and classified according to vegetable oil content (described by the term 'oil length') in three broad categories: short oil, medium oil, and long oil, roughly corresponding to <45%, 45–60%, >60% respectively. The variation in oil length is usually coincident with changes in the nature of the vegetable oil used and consequently the end use. Thus, for architectural gloss paint of maximum exterior durability, the alkyd binder will be a long oil alkyd based upon a drying oil such as linseed or soya bean oils (i.e. an unsaturated triglyceride oil). The drying oil provides the means by which the film former dries. In this case the conversion from a low molecular weight liquid polymer to a highly crosslinked solid arises as a result of oxidation. One characteristic of the long oil alkyd is that it is soluble in aliphatic hydrocarbons. In contrast the short oil alkyd is likely to be based on a saturated triglyceride (such as coconut oil). It will not be soluble in aliphatic hydrocarbons and will normally be dissolved in a high boiling aromatic. Although the short oil alkyd may be capable of forming a lacquer-

like film it would have a low softening point, and it is necessary to crosslink it in order to achieve a satisfactory film. In this case it is usually combined with an amino resin and crosslinked by condensation in a heat-curing process. It is debatable in this type of system whether the amino resin is crosslinking the alkyd or the alkyd is plasticizing the highly crosslinked amino resin. The former explanation is usually preferred because the proportion of the alkyd is invariably greater than that of the amino resin. The alkyd/amino resin ratio usually falls between 2:1 and 4:1 by weight. These types of system are used in industrial finishing. Alkyd/melamine formaldehyde compositions have found use in the automotive market for many years. Alkyd/urea formaldehyde compositions have found use in the domestic appliance market, although in both cases there have been new products developed that have displaced these materials to some extent, particularly when more stringent performance requirements have to be met.

Polyurethanes, urethane alkyds, and urethane oils

Structurally, these materials resemble alkyds in which polyester linkages are replaced partially or totally by urethane linkages.



Polyurethanes also include two-pack compositions for the industrial and refinish markets in which the curing is achieved by reaction between free isocyanate groups in one component and hydroxyl groups in the second component. The advantages of urethane oils and urethane alkyds are derived from the resistance of the urethane link to hydrolysis. In decorative (architectural) paints it is common practice to use binders which are a mixture of a long oil alkyd and urethane alkyd for maximum durability.

Amino resins

The most common types of amino resin are reaction products of urea or melamine (1:3:5 triamino triazine) and formaldehyde. The resins are prepared in alcoholic media, which enables the molecular weight and degree of branching to be controlled within practically determined limits related to the end use of the resin. The effect of this modification is shown in the solubility and reactivity of the resins so produced. The polymers produced are generally regarded as being derived from the hydroxymethyl derivatives of melamine and urea respectively; subsequent addition condensation and etherification reactions lead to complex, highly branched polymeric species. Curing or crosslinking to solid films (usually in combination with an alkyd or other polymer) can be achieved thermally (oven-curing) or at room temperature. In both cases the presence of an acid catalyst is essential if adequate and rapid cure is to be obtained.

The crosslinking capability of amino resins may also be utilized as a means of curing acrylic resins. In this type of film former a minor proportion (usually a few percent) of a monomer such as *N*-butoxymethyl acrylamide is incorporated into the polymer. This provides reactive sites which enable the acrylic copolymer to be crosslinked. A suitable choice of monomers allows the acrylic resin to be plasticized internally, so that the use of added plasticizers is avoided. These resins are of par-

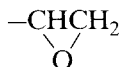
ticular interest where high levels of performance and particularly good adherence and flexibility are required.

Phenolic resins

The reaction of formaldehyde with a phenol gives rise to a range of resins that, in combination with other resins or drying oils, find use in industrial coatings. Broadly two main types of phenolic are produced, novolacs and resoles. Novolacs are low molecular weight linear condensation products of formaldehyde and phenols that are alkyl substituted in the *para* position. If the substituent alkyl group contains four or more carbon atoms (i.e. butyl or above — in the homologous series) the resin is likely to be oil-soluble. Resoles are products of the reaction of unsubstituted phenols with formaldehyde. Since the *para* position on the phenolic ring is available for reaction as well as the *ortho* position these resins are highly branched and can with continued reaction be converted into hard intractable glassy solids. Phenolics tend to confer chemical resistance to the compositions in which they are used. They are always used in combination with other resinous film formers. In some cases they may be prereacted with the other resin components, or they may be simply blended together. Thus a phenolic resin (e.g. a novolac) may be reacted with rosin or ester gum and then blended with a bodied (heat-treated) drying oil to form the binder in an architectural paint primer, or used simply in an unpigmented form as an oleoresinous varnish. Phenolic-based compositions find use in chemically resistant systems such as are required for pipes and tank linings.

Epoxide resins

The use of the epoxide or oxirane group



as a means of synthesizing resins and as a means of crosslinking binders is now well established. A large group of epoxide resins is based upon the reaction products of epichlorhydrin and bisphenol A (diphenylolpropane). These resins may be esterified with unsaturated fatty acids to give epoxy esters. These are film formers in their own right and resemble air-drying alkyds. They exhibit better chemical resistance than alkyds but are less durable than long oil alkyds in some circumstances. The way in which they break down may, however, be turned to good use, for example when used as 'self-cleaning' coatings. In this case the films may be pigmented with uncoated titania in the anatase form so that degradation in ultra-violet radiation causes erosion of the surface layers of the film, otherwise known as chalking. Such films gradually weather away, always presenting a white surface to the elements.

Epoxide resins may also be used in conjunction with melamine formaldehyde (MF) or phenolics, or they may be formulated into epoxy-alkyds, i.e. where they are effectively being used as polyols in admixture with less functional polyols such as glycerol. The epoxide group offers great versatility in curing, and a wide range of two-pack compositions are possible. One of the most popular methods of crosslinking uses the reaction with polyamides. This is the same method of cure as used in epoxy adhesive compositions. The crosslinking occurs as an addition of terminal amino groups of the polyamide to the epoxy group. This reaction occurs slowly at

room temperature. Crosslinking through the epoxide group can also arise from the use of polyamines or by means of the acid-catalysed polymerization to give ether crosslinks. It will be apparent that most of these products will be used in industrial applications.

Unsaturated polyesters

Unlike the previously described binders, unsaturated polyesters offer the benefit of totally polymerizable systems because the solvent in which they are dissolved is a polymerizable monomer. The simplest and most common polyesters are prepared from maleic anhydride/phthalic anhydride mixtures esterified with glycols such as propyleneglycol. The resins so produced are dissolved in styrene or vinyl toluene. The free radical copolymerization of the vinyl monomer and the maleic unsaturation in the polyester is usually initiated by a transition metal/organic hydroperoxide system at ambient temperature or by the use of the thermal scission of a diacyl peroxide at higher temperatures. Unsaturated polyesters have found extensive use both pigmented and as clears in the wood finish market. They are capable of widely divergent uses depending on their composition. Chemically resistant finishes for tank linings, for example, can be formulated on polyesters derived from isophthalic and terephthalic acids. Another class of chemically resistant finish is based upon chlorinated polyesters. In this case the polyester incorporates chlorendic anhydride in place of the more common phthalic anhydride.

Chlorinated rubber

Chlorinated rubber is a film-forming resin that is available in a wide range of molecular weights, from 3500 to about 20000. It is prepared by chlorinating rubber in solution, the commercial product containing about 65% of chlorine. It is used as the main binder in air-drying paints which are to be used in situations requiring a chemically resistant product of great durability. Because the polymer is a brittle solid, in paint applications chlorinated rubber requires plasticization. Chlorinated rubbers are also used in conjunction with other resins with which they are compatible, such as alkyls. Paints based on chlorinated rubber have been used for building, masonry, swimming pools, road marking, and marine purposes.

1.3.1.2 High molecular weight film formers

Almost all high molecular weight polymers are produced by the free radical initiated polymerization of mixtures of vinyl, acrylate, or methacrylate monomers. They may be polymerized in solution, in suspension or dispersion. Dispersion polymerization may be in hydrocarbon diluents (NAD) or in aqueous media ('emulsion polymers'). The reaction processes differ considerably between these systems as will become apparent when the subject is developed in Chapter 2.

One major exception to the foregoing is nitrocellulose. This material is formed by the direct nitration of cellulose in the presence of sulphuric acid. It is available in grades determined by the degree of nitration which, in turn, determine its solubility in various solvents. The grades used in refinish paints, wood-finish lacquers, etc. require the molecular weight of the original cellulose to be reduced somewhat, to meet viscosity requirements in the solvents commonly used.

In most cases the high molecular weight polymers do not need to be crosslinked in order to develop adequate film properties. A small number of solution polymers of moderately high molecular weight are, however, crosslinked through reactive

groups incorporated into the polymer chain. The physical properties of films produced from high polymers may be only marginally affected by the manner in which they were prepared or their physical form at the stage of film application. Thus automotive finishes derived from solution acrylics and NADs are virtually indistinguishable, albeit that the methods of application, processing conditions, etc. may be significantly different. In most cases the product that is selected will be dependent on the economics of the process overall rather than the product cost alone. The need to meet end use specification is the main reason for the similarity in film properties and performance of alternative product formulations.

Aqueous latexes (emulsion polymers) as a group have been one of the fastest-growing sectors of the paint market. Starting with the use of homopolymer PVA as a binder in matt and low-sheen decorative wall paints we have seen the development of more robust systems using internal plasticization (i.e. the incorporation of a plasticizing comonomer) and, more recently, the use of acrylic and methacrylic copolymer latexes. Improved performance has enabled the introduction of these paints into exterior masonry applications.

The most recent developments in this field have entailed preparing latex particles with specific morphologies, such as core/shell particles in which the particle cores may be crosslinked. These physical changes in the structure of the latex particles enable significant improvements to be achieved in the mechanical properties of the derived films, and in film integrity as measured by 'scrub resistance'. For industrial paint applications, functionalized polymers that will undergo crosslinking after coalescence have been developed. These compositions have low volatile organic content (VOC) and are thus 'environmentally friendly'.

1.3.2 Pigments

1.3.2.1 *Primary pigments*

Primary pigments comprise solid particulate material which is dispersed in the binder or film former described previously. We shall distinguish between them and supplementary pigments, extenders, fillers, etc. in that they contribute one or more of the principal functions, namely colour, opacification, and anti-corrosive properties. The supplementary pigments, extenders, although important, do not in general contribute to these properties to a major extent. Their function is related to reductions in cost, but they can contribute properties to a paint that may be less obvious than colour or opacity. Thus they may enhance opacity, control surface sheen, and facilitate ease of sanding.

The principal pigment in use is titanium dioxide. This is primarily because of reasons of fashion, e.g. in the decorative paint market there has been a tendency for white and pastel shades to gain greater acceptance over strong colours in recent years. The same is true to a lesser extent in other fields, such as the motor car industry. In this case early motor cars were painted black, and it was difficult to obtain cars in other colours. Nowadays it is the black car that is a comparative rarity. Titanium dioxide in its pigmentary form is a highly developed pigment. The high refractive index rutile form is most commonly used, and the pigment is manufactured within very close limits with respect to particle size and particle size distribution. Although normally regarded as being chemically inert the surface of the titanium dioxide crystal is photoactive, and the pigmentary form is surface coated to mini-

mize photochemical activity at the binder/pigment interface. Typical coatings contain silica and alumina in various proportions, and in addition to reducing photochemical activity they can improve the dispersibility of the pigment in the binder. Considerable research has been carried out into titanium dioxide pigments, and manufacturers are now able to offer a range of grades that are suitable for use in different types of paint media. The uses of titanium dioxide and other white pigments are detailed in Chapter 3, and its optical properties are discussed in Chapters 17 and 18.

Coloured pigments fall into two main groups, inorganic pigments and organic pigments. As a result of legislation governing the handling and use of toxic materials, many of the inorganic pigments traditionally used by the paint industry have been replaced by other less toxic materials. Thus except in a few industrial compositions lead pigments of all types (e.g. chromate, oxide, carbonate) have to a large extent been replaced, and it is to be expected that lead in all of its forms and chromates will ultimately be eliminated from all paints. Their removal from the scene gives rise to problems if a coloured pigment is used for the dual purposes of providing colour and contributing positively to the anti-corrosive properties of the paint film.

Some commonly used pigments are shown in Table 1.3. The selection and use of pigments is covered in detail in Chapter 3. The physics of colour are treated in Chapter 18 which includes a treatment of the principles and practice of colour matching. At one time colour matching was an art carried out visually by very skilful individuals. Whilst the skilled colour matcher has not been entirely replaced, there has been a gradual change to instrumental colour matching, a trend that has been accelerated by the development of sophisticated colorimeters and the use of the computer.

Table 1.3 — Some typical primary pigments

Colour	Inorganic	Organic
Black	Carbon black Copper carbonate Manganese dioxide	Aniline black
Yellow	Lead, zinc, and barium chromates Cadmium sulphide Iron oxides	Nickel azo yellow
Blue/violet	Ultramarine Prussian blue Cobalt blue	Phthalocyanin blue Indanthrone blue Carbazol violet
Green	Chromium oxide	Phthalocyanin green
Red	Red iron oxide Cadmium selenide Red lead Chrome red	Toluidine red Quinacridones
White	Titanium dioxide Zinc oxide Antimony oxide Lead carbonate (basic)	—

In automotive paints there has been a growth in the use of aluminium flake as a pigment to provide attractive metallic finishes. The dimensions of the flakes and their orientation within the paint film give rise to optical effects that cannot be achieved in other ways. Inevitably such paints are subject to problems in quality control, application, and colour matching that do not exist in solid colours. Nevertheless these problems are sufficiently well understood to be kept under control, and their continued use is amply justified aesthetically.

1.3.2.2 *Extenders, fillers, and supplementary pigments*

All three names have been applied to a wide range of materials that have been incorporated into paints for a variety of purposes. They tend to be relatively cheap materials, and for this reason may be used in conjunction with primary pigments to achieve a specific type of paint. For example it would be technically difficult and prohibitively expensive to produce satisfactory matt white emulsion paint using titanium dioxide as the only pigment. Titanium dioxide is not cost effective as a matting agent and indeed is not designed for this purpose. It is much more economic to use a coarse particle extender such as calcium carbonate in conjunction with TiO_2 to achieve whiteness and opacity in a matt or semi-matt product (e.g. a matt latex decorative paint, an undercoat or primer). Extenders do not normally contribute to colour, and in most cases it is essential that they be colourless. The particle sizes of extenders range from submicrometre to a few tens of micrometres; their refractive index is generally close to that of the organic binders in which they are used, and so they contribute little opacity from light scattering. Platelet type extenders such as wet-ground mica can influence the water permeability of films, and many therefore contribute to improved corrosion resistance. Talcs are often used (e.g. in automotive primer surfacers) to improve the sanding of the paint prior to the application of a topcoat. Many of the extenders in common use are naturally occurring materials that are refined to varying extents according to the use to which they are put. Whilst every attempt is made to ensure that they are reproducible they tend to be more variable and with a greater diversity of particle shape, size, and size distribution than primary pigments. A list of typical inorganic extenders is given in Table 1.4.

Table 1.4 — Some typical extenders

Chemical nature	Type
Barium sulphate	Barytes Blanc fixe
Calcium carbonate	Chalk Calcite Precipitated chalk
Calcium sulphate	Gypsum Anhydrite Precipitated calcium sulphate
Silicate	Silica Diatomaceous silica Clay Talc Mica

In recent years there have been several attempts to make synthetic (polymeric) extenders to meet special needs, in particular to replace some of the titanium dioxide in the paint film. One such material, 'Spindrift', originating from Australia, is in the form of polymer beads (spherical particles up to $30\mu\text{m}$ in diameter which incorporate submicrometre air bubbles and a small proportion of pigmentary titanium dioxide). The introduction of air bubbles into the polymer that forms the beads influences the light-scattering power of the titanium dioxide in one of two ways. It can reduce the average effective refractive index of the polymer matrix and so enhance the light-scattering of the titanium dioxide, if the bubbles are very small ($<0.1\mu\text{m}$). If the bubbles are large ($\sim 0.8\mu\text{m}$) they are able to scatter light in their own right. Other methods of introducing voids into paints in a systematic way to take advantage of the scattering of light by bubbles have included the emulsification of small droplets of a volatile fluid into aqueous latex paints which leave cavities within the film by evaporation after coalescence ('Pittment'); yet another is the use of non-coalescing latex particles in combination with coalescing latexes to give rise to cusp-like voids within the film (Glidden). All of these methods seek to achieve a cost-effective contribution to opacity without sacrifice of film integrity and other properties. These methods have received limited acceptance, mainly owing to economic reasons. Nevertheless, they do increase the opportunities open to the paint formulator to formulate a paint for a given purpose.

1.3.3 Solvents

Solvents are used in paint compositions for two main purposes. They enable the paint to be made, and they enable it to be applied to surfaces. This may seem to be stating the obvious, but it is important to appreciate that so far as the paint film performance is concerned the solvent plays no long-term role in this. This is not to say that in the early life of the film solvent retention does not affect hardness, flexibility, and other film properties.

The term solvent is used frequently to include liquids that do not dissolve the polymeric binder, and in these cases it is more properly called a diluent. The function of the diluent is the same as a solvent, as stated above. In water-based systems the water may act as a true solvent for some components, but be a non-solvent for the main film former. This is the case in decorative emulsion paints. More often in these cases it is common to refer to the 'aqueous phase' of the composition, acknowledging that the water present, although not a solvent for the film former, is present as the major component of the liquid-dispersing phase.

A wide range of organic liquids are used as paint solvents, the type of solvent depending on the nature of the film former. A detailed account of solvency, solvent selection, etc. is given in Chapter 4.

Considerable research effort has gone on into the study of the thermodynamics of solutions. This has provided the paint formulator with much more precise methods of solvent selection. The improved methods are based upon a better knowledge and understanding of molecular attractions in liquids and a recognition of the additivity of molecular attractions in mixed solvent systems. It is very rare for a single solvent to be acceptable in most situations, and the newer methods based upon solubility parameter concepts enable the more rational selection of solvent mixtures to meet a particular need.

Solvency alone is not the only criterion upon which solvent choice is made. Other important factors include evaporation rate, odour, toxicity, flammability, and cost.

These factors assume different degrees of importance depending on how the paint is used. If the paint is applied under industrial manufacturing conditions it is likely that problems associated with odour, toxicity, and flammability may be under control, but this is by no means certain. The need to install expensive extraction equipment or after-burners may preclude the use of some solvents and therefore some types of paint composition. Closely related to considerations of toxicity are those of pollution. Many countries have enacted legislation to protect the individual and the environment. This legislation has had a profound effect on the development of the paint industry and has influenced both the raw material supplier on the one hand and the paint user on the other. In North America there has been an enormous growth in water-borne systems at the expense of solvent-borne paints. This is a trend that is likely to continue.

Other alternatives to solvent-based paints are 100% polymerizable systems and powder coatings. In the former case a polymerizable monomer such as styrene fulfils the role of solvent for the composition, being converted into polymer in the curing reaction. With powder coatings, solvents may be used in the early stages of the paint-making process, but they are removed and recycled, so do not provide a hazard or problem for the user.

1.3.4 Paint additives

The simplest paint composition comprising a pigment dispersed in a binder, carried in a solvent (or non-solvent liquid phase) is rarely satisfactory in practice. Defects are readily observed in a number of characteristics of the liquid paint and in the dry film. These defects arise through a number of limitations both in chemical and physical terms, and they must be eliminated or at least mitigated in some way before the paint can be considered a satisfactory article of commerce.

Some of the main defects worth mentioning are settlement of pigment and skinning in the can; aeration and bubble retention on application; cissing, sagging, and shrivelling of the paint film; pigment flotation; and flooding. These defects represent only a small number of defects that can be observed in various paints. It is perhaps worth-while to describe cissing, shrivelling, sagging, flotation, and flooding here. They will be dealt with in more detail in Chapter 5, which describes some of the more common types of paint additives.

- ‘cissing’ is the appearance of small, saucer-like depressions in the surface of the film;
- ‘shrivelling’ is the development of a wrinkled surface in films that dry by oxidation;
- ‘sagging’ is the development of an uneven coating as the result of excessive flow of a paint on a vertical surface;
- ‘floating’ is the term used for the colour differences that can occur in a paint film because of the spontaneous separation of component pigments after application;
- ‘flooding’ (also known as ‘brush disturbance’) is the permanent colour change of a paint subject to shear after application.

To overcome these defects their cause requires to be understood and a remedy found. In some cases the defect may be overcome by minor reformulation. Shrivelling, for example, is commonly due to an imbalance between the surface oxidative crosslinking of a film and the rate of crosslinking within the film. This can usually

be overcome by changing the drier combination, which consists of an active transition metal drier such as cobalt which promotes oxidation and a 'through' drier such as lead or zirconium which influences crosslinking, but does not *per se* catalyse the oxidation process. In other cases simple reformulation will not provide a remedy, and specific additives have been developed to help in these cases. Thus anti-settling agents, anti-skinning agents, flow agents, etc. are available from specialist manufacturers for most defects and for most paint systems.

The problems of 'floating' and 'flooding' are associated with colloidal stability of the pigment dispersion and may arise from a number of different causes. The differential separation of pigment illustrated by floating occurs as a result of the differences in particle size of the component pigment and may be overcome by coflocculation of the pigments in the system. Another method of curing the condition may be to introduce a small proportion of a very fine particle extender such as alumina, of opposite surface charge to the fine particle pigment, to coflocculate with the latter.

The flooding (or brush disturbance) problem is indicative of flocculation occurring as a film dries. Under shear, as the brush disturbs the paint, the pigment is redispersed and the paint becomes paler in shade. This is because an increase in the back-scattering of incident light occurs, owing to the white pigment becoming deflocculated.

Cissing and sagging are illustrative of other aspects of physical properties associated with surface chemistry and rheology. In the former case, the effect is caused by a localized change in the surface tension of the film. In extreme cases this can give rise to incomplete wetting of the substrate, often distinguished by the term 'crawling'. Sagging, on the other hand, is a bulk property of the film that may be influenced by the colloidal stability of the composition. Ideal, colloiddally stable dispersions tend to exhibit Newtonian behavior, i.e. their viscosity is independent of shear rate. This means that on a vertical surface a Newtonian liquid that is of a suitable viscosity to be spread by a brush, i.e. with a viscosity of about 0.5 N s m^{-2} , will flow excessively unless the viscosity rises rapidly as a result of solvent loss. Alternatively, the paint formulator may aim to induce non-Newtonian behaviour such that the low shear viscosity of the product is very high. Thus, sagging may be avoided by either or a combination of these effects.

1.4 Paint making

Having considered briefly the most important constituents of paint, their function, and what they contribute to the final product, we need to consider the paint-making process. It is possible for a paint manufacturer to make almost all types of paint without any chemical processing. This is because each of the constituents can be purchased from a specialist manufacturer. Providing the paint manufacturer has certain basic plant capable of storing, mixing, dispersing, blending, and filling, he or she can be in business. Indeed some small volume or specialist manufacturers do just this, using basic formulations often provided by the resin or pigment supplier. However, the major paint manufacturers world-wide, seeking to capture a significant proportion of world markets, mount considerable research and development effort to produce products that are technically superior to those of their competitors or, if no better, can be produced more cheaply.

One of the most important parts of the paint-making process is the dispersion of

pigment to prepare a stable and reproducible product. This is usually carried out in two stages, the dispersion of the pigment in part of the binder solution (or other dispersing medium) to form a 'millbase', followed by blending ('second staging') with the remaining binder solution. Finally, minor components of the composition, such as driers, flow agents, solvent (to adjust the viscosity), and tinters (according to the requirements of colour matching) are added.

The dispersion process involves the wetting of the pigment with the dispersing medium, the separation of particles from their aggregated state and their stabilization in suspension, either as individual particles or in a lightly flocculated condition. The millbase is prepared in one of a number of mills (depending on the type of paint to be prepared), ranging from ball mills to cavitation mixers and attritors. Details of the processes involved and the types of mill that are available are given in Chapter 8.

1.5 Methods of application

There are four main methods of applying paint:

- by spreading, e.g. by brush, roller, paint pad, or doctor blade;
- by spraying, e.g. air-fed spray, airless spray, hot spray, and electrostatic spray;
- by flow coating, e.g. dipping, curtain coating, roller coating, and reverse roller coating;
- by electrodeposition.

The methods adopted depend on the market in which the paint is used, each type of paint being formulated to meet the needs of the application method. Spreading by brush or hand-held roller is the main method for applying decorative/architectural paints and the maintenance of structural steelwork and buildings generally. It is also important in marine maintenance, although other methods (e.g. airless spray) may be used during the construction of a ship.

Application by spraying is the most widely applicable method. It is used for painting motor cars in the factory and by refinishers following accident damage; it is used in the wood-finishing industries (e.g. furniture) and in general industrial paints (e.g. domestic appliances). The various forms of spray painting make it a particularly versatile method of application. The flow coating methods are limited essentially to flat stock (e.g. chipboard) and coil coating (aluminium or steel coil) where they are much valued because of the high rates of finishing that can be achieved.

Electrodeposition has become established as the main method of priming the steel body shells of motor cars. The total process which involves degreasing, phosphate treatment, electrodeposition of primer, and then spray application of surfacer and finishing coats has raised the standards of corrosion resistance and general appearance considerably during this period. Electrodeposition may take place with the car body acting as either the anode or the cathode. In recent years it has been claimed that cathodic forms of electropaint give the better corrosion protection.

Mainly because of environmental considerations, powder coating has been a major growth area in industrial finishing, particularly in Western Europe, which produced 53% of the total world market for powder coatings in 1993. Powder coatings are normally applied by electrostatic spray, with minimal overspray losses and without the emission of VOCs.

Table 1.5

Market	%
Car manufacture	10.7
Car refinishing	6.3
Metal manufactured goods (inc. drum and can coatings, domestic appliances)	36.8
Woodfinishes	16.9
Marine and offshore	11.2
Industrial construction and maintenance	11.3
Other	6.8

Source: EC Report, *Reduction of VOC Emissions from Industrial Coating of Metal Surfaces*, Warren Spring Laboratory, September 1991.

The methods of application will be described in the appropriate chapters, discussing each of the main market areas.

1.6 Paint markets

It is convenient to discuss the markets for paint in terms of products for specific end uses. The end use determines the nature of the coating or system required to fulfil property requirements, such as mechanical properties, durability and chemical resistance properties related to the use of the article coated, which vary from an ocean-going liner to a beverage can. Thus, specialized products may be manufactured by small specialist paint companies; geographical considerations may be taken into account in some instances so that the user can exercise closer control over the continuity of supply and quality of the coatings purchased.

The principal markets for paints are the decorative (household or architectural) paints market and the widely divergent industrial paint markets. The requirements of the former are met by two types of composition based on autoxidative resin systems and latex paints; the technology of industrial coatings is more diverse in terms of film property requirements, methods of application and cure. In the majority of industrial coating operations the application methods and curing processes are thus carried out under factory conditions, under which greater control can be exercised.

Some idea of the scale of paint manufacture can be obtained from statistics published by a number of organizations world-wide. For example, the total EC industrial coatings market (1991) was 2390000 tonnes per annum (Table 1.5).

It is interesting to note that four countries within Europe consume almost 75% of the industrial coatings produced — Germany (28%), Italy (18%), the UK and France (about 13% each). The leading paint manufacturing countries in the world are all to be found in the Far East — Japan (2090000 tonnes), China (940000 tonnes), South Korea (430000 tonnes), Taiwan (280000 tonnes), and the Philippines (230000 tonnes) (source: National Statistics, 1992).