

3

Pigments for paint

A G Abel*

3.1 Introduction

This chapter introduces pigment technology and is designed for the newcomer to the paint industry, who has some chemical knowledge. It is intended to be comprehensive, but can only provide an introduction to the aspiring paint technologist, or someone closely connected to the paint industry. Other publications, including suppliers' literature, go into greater detail.

In this chapter, pigments will be defined and their required qualities detailed. The methods of classification and the terminology used in the paint industry are explained. Pigment manufacturing methods are outlined and reference is made to their environmental and toxicological properties, with implications for the paint industry. A description is given of the application properties of pigments, with advice on the rules to be adopted in order to select the correct pigments for use in paint.

Finally, there are brief descriptions of the more important pigment types used in paint, grouped in colours, with special mention of other pigments which are used to obtain special properties such as corrosion inhibitors, extenders, aluminium, and pearlescent pigments.

3.2 Definition

The word 'pigment' derives from the Latin *pigmentum* — *pingere*, to paint. An internationally accepted [1, 2] definition has been provided by the Color Pigments Manufacturers Association of America (CPMA, but formerly known as Dry Color Manufacturers Association of America, DCMA):

colored, black, white or fluorescent particulate organic or inorganic solids, which are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in

*Based on original chapter by Miss J F Rollinson.

which they are incorporated. They alter appearance by selective absorption and/or scattering of light. Pigments are usually dispersed in vehicles or substrates for application, as for instance in the manufacture of inks, paints, plastics, or other polymeric materials. Pigments retain a crystal or particulate structure throughout the coloration process.

This definition concentrates on the products used to give an aesthetic effect, such as colour or opacity, but there are other types of pigment that are used for specific purposes, such as 'extenders'. Extenders do not usually affect the colour or opacity of a paint film, but may play an important role in the film properties such as reinforcement, gloss (usually to make the film less glossy), hardness, etc. They can also affect the properties of the paint itself, such as its rheological properties, settling characteristics, or simply its cost. Extenders play an important part in paint formulation so some of the important types are described in Section 3.12.11.

Finally there are pigments that may affect the appearance of the film, but are primarily used for other properties such as fire retardance, corrosion protection, or to improve the weatherability of the substrate, mainly by absorbing ultraviolet light or other harmful radiation.

Just to confuse, the term pigment is also used for substances that give colour to animal and vegetable tissue. These biological pigments have no connection to the pigments described in this chapter; many are in fact dyes.

If we break down this definition we can recognize the essential requirements of a pigment.

3.3 Required qualities of pigments

3.3.1 Appearance

Most pigments are used to provide a visual effect, mainly colour and opacity. Having achieved the required colour and opacity, it is also important to ensure the pigment will remain essentially insoluble in the system in which it is used and will give the required physical properties, such as light fastness, weatherability, and resistance to chemicals. The paint technologist must meet these criteria and is usually expected to do so within the economic restraints imposed by the end application.

3.3.2 Colour of pigments

The colour of a pigment is mainly dependent on its chemical structure. The selective absorption and reflection of various wavelengths of light that impinge on the pigmented surface determines its hue (i.e. whether it is red or yellow, etc.). A blue pigment appears so because it *reflects* the blue wavelengths of the incident white light that falls upon it and absorbs all of the other wavelengths. Hence, a blue car in orange sodium light looks black, because sodium light contains virtually no blue component. Black pigments absorb almost all the light falling upon them, whereas white pigments scatter and reflect virtually all the visible light falling on their surfaces. Fluorescent pigments have an interesting characteristic. As well as having high reflection in specific areas of the visible spectrum, they also absorb light in areas outside the visible spectrum (the ultraviolet part where our eyes are unable to detect), splitting the energy up, and re-emitting it in the visible spectrum. Hence, they appear to emit more light than actually falls upon them, producing their brilliant colour.

The differing absorption and reflection characteristics of compounds are attributed to the arrangements of the electrons within their molecules and to their energy and frequency vibration. A molecule will absorb electromagnetic radiation from part of the spectrum. This absorption excites the electrons, resulting in the promotion of an electron from its ground state, E_1 , to an orbital of higher energy E_2 . The wavelength of the light absorbed is determined by the difference in energy E between the two orbitals concerned:

$$E = E_2 - E_1 = hc/\gamma$$

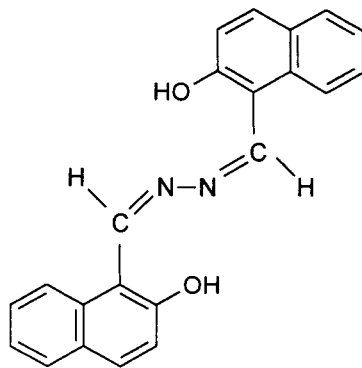
where h is Planck's constant, c is the velocity of light, and γ is the wavelength of light.

A given molecule has a limited number of orbitals, each with its own characteristic energy. This means that the energy difference E described above has certain definitive values. The pigment molecule is therefore only able to absorb light at particular wavelengths, determined by the energy difference E — that is characteristic of the given molecule. As the electronic excitation is accompanied by a multitude of rotational and vibrational transitions, the absorption is not at a single wavelength, but over a wide band. The wavelengths not involved in the absorption are reflected and determine the colour of the molecule, and therefore produce the complementary colour to the wavelengths absorbed.

3.3.2.1 Fluorescent pigments

Most pigments described as fluorescent do not fit our definition. They are fluorescent dyes that have been dissolved into a resin, often achieving good migration fastness on account of their reacting with the resin. The dyes themselves are often basic dyes, with poor light fastness, and while as 'pigments' they have improved durability, nevertheless they are still considered poor and are limited to interior applications. They also have poor opacity and are quite expensive.

There is an exception, azomethine (CI Pigment Yellow 101), which is a true pigment and has been known since the end of the nineteenth century. It finds little use in the paint industry, but its structure is interesting, especially when one considers the importance of conjugation (qv) in a molecule to develop colour.

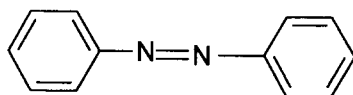


CI Pigment Yellow 101 reference CI 48052 'Azomethine'

3.3.2.2 Coloured organic compounds

For organic compounds it has been found that certain groups of atoms are essential for colour. These groups are known as chromophores. Colour is more or less limited to aromatic compounds. An exception is the important coloured aliphatic compound, lycopene, which is responsible for the red colour of tomatoes. The molecule consists of a long hydrocarbon 'conjugated' chain; this is, consisting of alternate single and double bonds. This allows free movement of the electrons giving rise to the absorption of light as previously described and hence colour [3].

Obviously, the nature of the benzene ring gives many more opportunities for conjugation, therefore most coloured organic compounds contain benzene rings and are thus aromatic in nature. Even nitrobenzene is slightly coloured. The azo group, --N=N-- (and its tautomers), also provides a very good linkage, maintaining a conjugated system, hence azobenzene is coloured, especially in solution.



Azo Benzene

Additional substituents on the molecule, known as auxochromes, can modify the colour by donating or accepting electrons. Substituents that donate electrons usually have lone electron pairs, e.g. alkoxy, hydroxy, alkyl and arylamino groups, whereas groups that can accept electrons include NO_2 , COOH , COOR , SO_2 [4, pp. 12–15].

More details regarding the colour of organic compounds can be found in reference [5].

3.3.2.3 Coloured inorganic compounds

Colour in inorganic pigments is more difficult to explain, partly because no single theory fully accounts for what is observed. The main cause of colour is due to charge transfer spectra and/or d–d transition spectra, especially of the 3d transition metals. However, this does not explain all inorganic pigments. It is well known that molecules containing a metal in two valency states can be intensely coloured, e.g. Prussian blue (CI Pigment Blue 27). It is thought that the deep colour of such compounds is due to transfer of an electron from ions in the lower valency state to a higher one.

Another cause of colour is the trapping of a cation in the three-dimensional lattice carrying a negative charge. Therefore, within these cavities there is room for positive and negative ions and neutral molecules. Ultramarine (CI Pigment Blue 29) is an example of such a molecule.

A very detailed account of colour in inorganic compounds appears in reference [6].

3.3.2.4 Other factors influencing colour

It is not only the pigment's chemical nature that determines its colour. The crystal structure is now recognized as playing an important role. Several pigments can exist in more than one crystal form, a property known as polymorphism, and these forms

can be of very different colours. The clearest examples are linear *trans*-quinacridone, CI Pigment Violet 19, which exists in three different crystal forms (see Section 3.12.6.9), and copper phthalocyanine, which exists in several different forms (see Section 3.12.8.4). Polymorphism is not limited to organic pigments. Titanium dioxide exists in three crystal forms and other polymorphic pigments such as lead chromates and lead molybdates also have more than one crystal form.

Particle size also influences colour. Smaller particles are usually brighter in shade and change the hue of a pigment. As a general rule, smaller particles give:

- greener yellows;
- yellower oranges;
- yellower reds up to mid red;
- bluer reds from mid reds;
- redder violets;
- greener blues;
- yellower greens.

The effect of the crystal structure and particle size on colour is well covered in reference [7].

Pigment manufacturers have become very skilled in producing pigments with the desired crystal form and even with a narrow particle size distribution in order to impart the desired colour, physical properties, and hence performance.

3.3.3 Tinctorial strength

As well as colour, tinctorial strength must be considered when choosing a pigment. The higher the tinctorial strength, the less pigment is required to achieve a standard depth of shade, therefore it has economic implications. The chemical structure is fundamental to the tinctorial strength of the pigment molecule. In the case of organic pigments the colour and tinctorial strength are dependent on the ability to absorb certain wavelengths of light and in turn this is related to the conjugation in the molecule. Highly conjugated molecules show increased tinctorial strength. Therefore, increasing the aromaticity of the molecule, promoting a planar molecule and the addition of certain substituents into the molecule, mainly electron donors as described earlier (see Section 3.3.2) all encourage high tinctorial strength.

Inorganic pigments that are coloured because of their having metals in two valency states, show high tinctorial strength, whereas those that have a cation trapped in a crystal lattice are weakly coloured.

Particle size can make a dramatic difference to the tinctorial strength of a pigment, smaller particles yielding higher tinctorial strength. Manufacturing conditions are the main factor in influencing the particle size of pigment crystals, so pigment manufacturers play a crucial role. They can reduce the size of the particles by preventing the growth of crystals during synthesis. Rosin is often used for this purpose, particularly in pigments intended for the printing ink industry, but more sophisticated techniques have to be used for higher-quality pigments. The paint manufacturer can increase tinctorial strength by efficient dispersion, which is particularly important for pigments with a very small particle size. However, it is not usually possible to reduce the size of the primary crystal particles during the dispersion process.

3.3.4 Particulate nature of pigments

Pigments can be either crystalline or non-crystalline (amorphous), i.e. the atoms within each pigment molecule are arranged in either an orderly or random fashion respectively. From our definition of *pigment* we have described them as maintaining a particulate structure throughout the coloration process and as being insoluble. Therefore the following colorants *cannot* be considered pigments.

3.3.4.1 Solvent soluble dyes

Some colorants do dissolve during their incorporation into a binder and then return to an insoluble form, or are held within the crystalline structure of the binder. These colorants cannot be strictly considered pigments. Most are considered to be solvent soluble dyes. They are frequently used for the coloration of plastics. Other solvent soluble dyes, usually metal complexes, are used for the coloration of solvent-based packaging inks and clear lacquers. Their high transparency, high-colour strength, and brilliant, strong shades are particularly useful when printing on aluminium foil. They have to be dissolved in specific solvents, usually alcohols, ketones, or esters. It is this limited solubility and sometimes their low fastness properties that often limit their application. There are also some relatively simple 'solvent soluble dyes' that are soluble in hydrocarbons, including some plastics and waxes. They have poor light fastness and cannot be overcoated, as they dissolve in the top coating, thus severely limiting their application.

In the textile industry, a number of colorants would be found to be insoluble within the fibre.

3.3.4.2 Vat dyes

Vat dyes are highly insoluble, but to apply them to a fibre they are dissolved by reduction with powerful reducing agents, forming the so-called soluble leuco form, which is then used to dye the fibre. Oxidation follows, converting the dye to the insoluble form within the fibre. Because the colorant has gone through a soluble stage it cannot be considered a pigment. However, several compounds that are used as vat 'dyes' can also be used directly as pigments, by eliminating this solubilizing process, for example CI Vat Orange 7, which is also CI Pigment Orange 43.

3.3.4.3 Disperse dyes

Disperse dyes are mainly used for the coloration of polyester fibres. They are *almost* insoluble, but have to have a slight solubility. When put into a dyebath, they have to be dispersed, usually with the help of surface-active agents. A small proportion of the dye goes into solution. However, the dye prefers to be in the polymer phase, and therefore enters the fibre. Equilibrium is re-established by more dye going into solution, once again entering the fibre. In this way the depth of the dyeing builds up, usually at temperatures above 100°C obtained by dyeing under pressure. Again, as they go through a soluble stage, they cannot be considered pigments. Several disperse dyes can also be used as solvent soluble dyes.

3.3.4.4 Azoic dyes

These include some of the oldest known dyes, owing their origin to the textile industry. In 1880, Read Holliday in Huddersfield (later to become part of ICI, now Zeneca) patented its 'developing dyes'. It found that cotton impregnated with naphthol (2-naphthol) and dried, could then be passed through a liquor of an ice-

cold diazonium compound. It was in fact synthesizing a pigment inside the fibre and consequently produced a cloth with very good fastness properties. But again the colorant is not a pigment as it does not remain insoluble throughout the coloration process.

3.3.5 Insolubility

In the definition of a pigment, it was stated that it must be 'insoluble in, and essentially physically and chemically unaffected by the vehicle or substrate'. Therefore, when a pigment is incorporated into our paint formulation, it must not significantly dissolve in either the vehicle or solvents. Nor must it react with any of the components, such as crosslinking agents. Pigments are required to retain these properties even when the paint is being dried, which is frequently carried out at elevated temperatures. Once in the dried film the pigment must also remain unaffected by the substrate and to agents with which it comes into contact, including water, which may simply be in the form of condensation, or acidic industrial atmospheres.

Although we have defined pigments as being insoluble, in practice they may dissolve under certain conditions leading to application problems. Organic pigments may dissolve to a limited extent in organic solvents, and although inorganic pigments are completely insoluble in such solvents, other chemicals may still affect them. The application problems associated with a pigment being soluble in a system include the following.

3.3.5.1 *Blooming*

If the pigment dissolves in the solvent, as the paint dries, the solvent comes to the surface and evaporates, leaving crystals of the pigment on the surface in the form of a fine powder. This deposit looks very much like the bloom seen on the surface of soft fruit — hence its name. As solubility increases with temperature, this phenomenon is made worse at elevated temperatures, such as in stoving paints. As the pigment has also dissolved in the binder, usually in the form of a supersaturated solution, it continues to migrate even when the solvent has evaporated and continues to appear on the surface even after being wiped clear.

3.3.5.2 *Plate out*

The effect of plate out looks similar to blooming, but occurs in plastics and powder coatings. However, it is not due to the pigment dissolving, but rather to the surface of the pigment not being properly wetted out. It usually occurs mainly with complex pigments and once wiped from the surface does not reappear.

3.3.5.3 *Bleeding*

Pigments in a dried paint film may dissolve in the solvent contained in a new coat of paint applied on top of the original film. If this topcoat is the same colour this will be of little consequence. However, if the topcoat is a different colour, particularly a white or pale colour, the result can be disastrous. It is most noticeable when a white paint is applied over a red paint. The red pigment bleeds into the new white paint film, staining it pink. Subsequent coats will not cover the original, as the pigment continues to dissolve. Again elevated temperatures exacerbate the problem. Although usually associated with red pigments, it is possible with any pigment possessing only poor to moderate solvent fastness.

3.3.5.4 Recrystallization

This phenomenon was almost unknown until the introduction of beadmills. During the milling stage heat is generated, which dissolves a portion of the pigment. The paint often goes through quality control without a problem, appearing strong and bright, because the pigment is acting as a dye in a supersaturated solution. However, over a period of time the dissolved 'pigment' starts to precipitate out, losing brilliance and colour strength. This becomes especially noticeable in the case of paints containing two differently coloured pigments, e.g. a blue and a yellow, that have different solubility characteristics. The more soluble yellow pigment dissolves and then as it comes out of solution and precipitates, the paint will go bluer in shade. Recrystallization can even take place in aqueous systems. It can be avoided by using less soluble pigments and/or by controlling the temperature during the dispersion process.

3.3.5.5 Imparting insolubility into an organic molecule

Insolubility can be imparted to a molecule in a number of ways; however, most of them increase costs, and therefore it is a property that is critical for the optimum economic performance:

- *Increasing molecular size* decreases solubility, therefore in general the more complex the pigment, the better is its resistance to solvents. However, just building up the size of the molecule is likely to have other effects, such as reducing tinting strength and increasing costs, so it would be unlikely to be an efficient method on its own.
- *Adding certain substituents* can either increase or decrease a pigment's insolubility. Long chain alkyls, alkoxy, alkylamino, and acids such as sulfonic acid groups all increase solubility, whereas insolubilizing groups include carbonamide ($-\text{CONH}-$), nitro, and halogens. These groups have proved particularly effective for the so-called 'azo' pigments.
- *Introducing a metal group* reduces solubility. The formation of metal salt with certain water-soluble dyes that contain carboxy acid or sulpho groups can make the colorant insoluble. The more acid groups in the dye, the better the solvent fastness obtained. This is a relatively cheap method, but such pigments, known in Europe as *toners*, have a limited application in paint because of their poor resistance to chemicals. Several new and more complex toners have been recently introduced for the coloration of plastics. The introduction of metal groups by the *formation of metal complexes*, where the bond is covalent also produces pigments that are highly insoluble.
- *Intermolecular bonding* can often result in pigments having much better resistance to solvents than one would expect from their molecular structure. The best example of such a pigment is linear *trans*-quinacridone (CI Pigment Violet 19). If the shape of the crystal does not allow the formation of secondary bonding (i.e. the α crystal modification), the molecule does not have good resistance to solvents, whereas the β and γ modifications have excellent solvent fastness.

3.3.5.6 Testing solvent resistance

The bleed resistance can be tested by overcoating the pigmented paint with a white paint. Normally, either a nitro-cellulose lacquer or stoving paint is used for this test. Fastness to individual solvents can be tested by incorporating a small amount of

pigment into an envelope of filter paper, then immersing in solvent for a given amount of time. The staining of the solvent is compared with a standard iodine/potassium permanganate solution. Rating 5 indicates no staining, whereas severe staining is rated 1. For quality control purposes a representative solvent blend can be used.

3.3.6 Opacity

The terms 'hiding power' and 'opacity' are often interchanged, but there is a subtle and important difference. Hiding power is the ability of a pigmented coating to obliterate the surface. It is dependent on the ability of the film to absorb and scatter light. Naturally, the thickness of the film and the concentration of the pigment play a fundamental role. The colour is also important: dark, saturated colours absorb most light falling upon them, so blacks and deep blues cover up the surface, whereas yellows do not. Yet carbon black and most organic blue pigments are quite transparent, because they do not scatter the light that falls on them. At the other extreme, titanium dioxide absorbs almost no light, yet its ability to scatter light ensures that at a high enough concentration it will cover the substrate being coated. In practice a combination of pigments is often used in order to obtain optimum results.

In most coating systems we want to obliterate the surface, but there are certain applications where this is not the case. This is particularly true of printing ink applications, where high transparency is often a necessity. Even certain types of paint may require transparency, especially wood finishes, certain can coatings and in metallic and pearlescent finishes, now so popular in automotive finishes.

A key factor in the opacity of a pigment is its *refractive index* (RI), which measures the ability of a substance to bend light. The opacifying effect is proportional to the difference between the refractive index of the pigment and that of the medium in which it is dispersed. This is one of the main reasons why titanium dioxide is now almost universally used as the white pigment in paint. In Table 3.1 the refractive index is given for white pigments, important extender pigments, and for media in which they may be incorporated. It explains why titanium dioxide gives such good opacity and why extender pigments are transparent or nearly so.

The refractive index is fundamental to a given compound providing it retains the same crystal structure. As most inorganic pigments have a high refractive index and organic pigments have much lower values, it follows that most inorganic pigments

Table 3.1

Medium	RI	Pigment or extender	RI
Air	1.0	Calcium carbonate	1.58
		China clay (aluminium silicate)	1.56
Water	1.33	Talc (magnesium silicate)	1.55
		Barytes (barium sulphate)	1.64
		Lithopone 30% (zinc sulphide/barium sulphate)	1.84
Film formers	1.4–1.6	Zinc oxide	2.01
		Zinc sulphide	2.37
		Titanium dioxide: Anatase	2.55
		Rutile	2.76

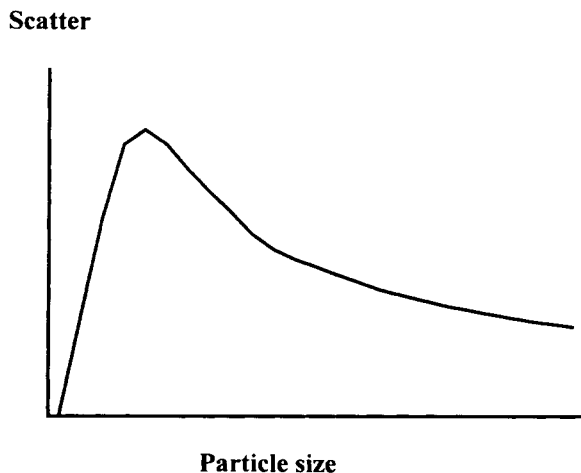


Fig. 3.1 — The effect of particle size on the ability of a pigment to scatter light.

are opaque, whereas organic pigments are transparent. If the refractive index was the only factor affecting opacity this would always be the case, but there is another factor that also plays an important role, the particle size of the pigment — or more correctly the particle size distribution. As the particle size increases, the ability of the particle to scatter light increases, up to a maximum (see Fig. 3.1). It then starts to decrease. This ability to scatter light increases the hiding power of the pigment, and therefore the hiding power also reaches a maximum and then decreases as the particle size increases.

Whereas the refractive index of a compound cannot be altered, the pigment manufacturer can influence the particle size of pigments; consequently particle size selection has become one of the principal developments in pigment technology in recent years.

The particle size that gives optimum opacity can be calculated for any given wavelength [4, pp. 129–133]. For maximum opacity, the desired particle size is approximately half the dominant wavelength. A whole series of organic pigments is now available in which the particle size has been made as near as possible to this optimum point. As these particles are considerably larger than conventional pigments, they also have a lower surface area and therefore less binder demand. So not only are such pigments inherently more opaque, but it is possible to use them at higher concentrations without adversely affecting flow properties, gloss, or weatherability. Indeed the lightfastness and weatherability are much improved. The disadvantage of such pigments is that they have much reduced tinctorial strength, but as they are usually intended for full and near full shade paints, where one cannot use the even more opaque titanium dioxide, this is not such a problem.

There has even been the development of organic pigments that have even larger particles, moving them beyond this point of maximum opacity, in order to combine transparency with the higher light fastness one sees from larger particles. This phenomenon has been called 'ultra transparency', but has the disadvantage that such pigments have low tinctorial strength.

The techniques used to manufacture pigments in as narrow a particle size distribution as possible are published and depend on dissolving the pigment in various solvents, at elevated temperatures and pressures, then recrystallizing under carefully controlled conditions [8].

As titanium dioxide is used for its covering power, many studies have been undertaken to determine how this property can be optimized. Whereas organic pigments have a particle size of between 0.1 and 0.5 μm , inorganic pigment can be much larger. Therefore titanium dioxide manufacturers often try to reduce the size of their pigment particles, down to around 0.25 μm , thereby enhancing opacity. Crystal size also plays a role, as does the state of dispersion and, needless to say, pigment concentration [9].

3.3.7 Transparency

Usually, transparency is obtained by producing as small a pigment particle as possible. This is achieved by surrounding the particles as soon as they are formed with a coating, which prevents the growth of crystals. The most common products used for this coating are rosin or rosin derivatives [10]. Rosin is a natural product, whose main constituent is abietic acid. It is often reacted with alkalis, such as sodium hydroxide, to form alkaline earth metal rosinate. This is particularly useful for printing ink pigments that are required to have high transparency and it has the added advantage that such pigments are more easily dispersed. For higher-quality pigments that are required to have better mechanical stability, alternative coatings such as more complex rosin derivatives with higher melting points and greater resistance to oxidation or other surface treatments are used.

There is an important group of transparent inorganic pigments. Although iron oxide pigments are normally opaque, they can be made in a transparent form. The transparent form is widely used for metallic finishes, where its high transparency not only gives an attractive finish, but its excellent weatherability can actually improve the weatherability of pigments with which they can be combined. This is known as a synergistic effect. Transparent iron oxides depend on the particles being unusually small, and also having a specific crystal shape.

The dispersion process can influence the transparency obtained, as it consists of breaking up clusters of particles to individual primary particles. However, dispersion does not break down these primary particles, which are the result of the pigment's manufacturing process, so all one can do is to make maximum use of the pigment's inherent particle size. Good dispersion will make maximum use of a small particle's transparency.

3.3.7.1 *Measurement of transparency and opacity*

Transparency is simply assessed by applying the coating over a black and white contrast chart and measuring the colour difference. The greater the colour difference, the higher the transparency.

Covering power is measured in a similar way, but is normally expressed in terms of what film thickness achieves complete obliteration of the surface. Therefore, the coating is applied in a wedge shape over a contrast chart. The film thickness is built up over the length of the chart, which is attached to a metal panel. The point at which complete obliteration is observed is noted and the film thickness at that point measured.

3.3.8 Durability

For most paint applications, pigments are required to be durable. They should neither fade nor darken to any extent, a function not just of the pigment but of the whole system. The pigment concentration and other pigments used in the paint play a role. Durability must also be considered in terms of the end use. Clearly an automotive paint must have very much better light and weather fastness than the paint on a gardening or kitchen tool.

Pigments must not weaken the film formed by the binder. Indeed, in a well-formulated paint it is likely to assist in producing a cohesive, hard, elastic film, protecting the substrate and increasing the life expectancy of the paint film. This will also be dependent on whether the paint film is sufficiently thick, another property that can be influenced by correct pigmentation.

For corrosion-resistant paints, the pigment is a fundamental component, often providing chemical protection to the substrate. Strictly speaking this contradicts the definition of a pigment. It would be impossible to do justice to such pigments in a single chapter; indeed corrosion inhibition is a technology in its own right.

3.3.8.1 *Light fastness*

When considering light fastness one must look at the whole pigmented system, not just the pigment. The binder imparts a varying degree of protection to the pigment, so the same pigment will tend to have better light fastness in a polymer than it will in paint. Even within paints, one generally finds that a pigment's light fastness improves from an aqueous emulsion system, through an air-drying alkyd to an acrylic/melamine formaldehyde system. Pigments will nearly always have a much poorer light fastness in a printing ink system, where there is less resin to protect the pigment and there is a double effect of light passing through the pigmented layer, being reflected by the substrate and back through the pigmented layer. Similarly, metallic finishes are more prone to fading than solid colours and hence are often overcoated with a clear resin containing an UV absorber.

Other pigments may also play a role in a pigmented system. Titanium dioxide promotes the photodegradation of most organic pigments, so the higher the ratio of titanium dioxide (i.e. the paler the shade), the worse the light fastness. On the other hand iron oxide appears to improve the light fastness of organic pigments, probably because it is an effective absorber of UV light. If two pigments together give a better light fastness than one would expect it is called a synergistic effect, where they are lower, it is called an antagonistic effect.

A few inorganic pigments are unchanged by exposure to light, but most pigments and all organics are changed in some way. This may show itself as darkening on the one hand or complete fading on the other. The energy responsible for fading is sometimes mistakenly believed to be exclusively UV light. This is not always the case: certain pigments may appear to have good fastness in UV, but fade on outdoor exposure, and vice versa. While the chemical constitution plays a fundamental role in a pigment's ability to resist light, other factors such as the pigment concentration, the crystal modification, and the particle size distribution have an effect. Additionally, other factors in the environment can dramatically affect results, such as the presence of water and chemicals in the atmosphere or in the paint system. Hence the light fastness of a pigmented system can only truly be tested in the final formulation and application. Light fastness tests must be carried out only under carefully controlled test conditions. Therefore, much effort has gone into perfecting a

test system that will give as meaningful results as possible when evaluating the light fastness of a pigmented system.

3.3.8.2 *Light source*

Although natural daylight would be the ideal, it is normal to try to accelerate the test by using an intense source of light that corresponds as closely as possible to natural daylight. One of the most commonly used light sources is the xenon arc lamp, which can be further improved by filters, which screen out certain parts of the UV spectrum. As the xenon lamp ages, the lamp's energy distribution changes, so it is important to follow manufacturers' instructions regarding the life of the lamp. Control of humidity is essential when testing light fastness.

3.3.8.3 *Blue Wool Scale*

Light fastness is quantified by exposing the sample alongside a Blue Wool Scale and comparing the fading obtained with the sample with the strip of wool showing similar fading. The Blue Wool Scale consists of eight strips of wool all dyed with standard dyes. In theory, strip 1 fades twice as fast as 2, which fades twice as fast as 3, etc. Therefore, a difference of two points is a four-fold difference and three points is an eight-fold difference, etc. In practice this is not quite the case especially at the top end of the scale, where most paints are needed to be, but it is a good guide. It can also be difficult to assess the light fastness of a glossy paint film with a textile substrate, which can be of a completely different colour and depth of colour. Work is going on to try to develop the use of printed strips, but there are problems, particularly at the lower end of the scale. It is also agreed that certain modern paint systems, such as automotive and coil coating systems, need a light fastness in excess of eight, and therefore require an extended scale.

Ratings are based on the 1–8 scale, where 1 is poor and 8 is excellent. Interim steps can be indicated, e.g. 5–6 and darkening can be denoted by 'd' after the figures.

3.3.8.4 *Weatherability*

Although closely related to light fastness, weatherability adds the extra dimension of atmospheric conditions, including salt from the sea, waste gases from industrial areas, or very low humidity from desert conditions. It is therefore necessary to include in any weatherability data the exact conditions of exposure. Machines are available which in addition to a xenon lamp, include wet cycles interspersed between longer dry cycles, depending on the exposure anticipated.

Weatherability is designated in terms of the 1–5 Grey Scale, where 5 is no change, and 1 is a severe change. To repeat, as well as the figure it is necessarily to denote the place and period of exposure, if necessary with a note about the prevailing conditions.

3.3.8.5 *Effects of chemistry on light and weatherfastness*

Light fastness in organic molecules, especially azo pigments, usually increases with increasing molecular weight. A planar molecular structure also promotes light fastness, probably due to intermolecular bonding, as exemplified by linear *trans*-quinacridone, where the β and γ modifications have much better fastness properties than the α form. Polycyclic pigments with a symmetrical structure generally have high fastness, e.g. phthalocyanine, quinacridones, perylenes, and carbazole violet.

Additional groups can be introduced into organic, especially azo pigment molecules, which increase the light fastness. Chlorine groups invariably improve light fastness. Other groups that have a positive effect include $-\text{NO}_2$, $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{CONH}-$, $-\text{SO}_2$, and $\text{NH}-$.

3.3.9 Chemical stability

The requirements of a pigment to withstand any chemicals with which it may come into contact may well be a critical factor in the selection process. One has to consider two aspects of chemical attack. First it can come from within the paint itself. The resin, crosslinking agents, UV-initiators, and any other additive may react with the pigment and change its performance. In the early days of UV-cured coatings, additives on the pigment drastically reduced storage stability, resulting in the coating gelling in the can. One has to be very careful when selecting pigments for powder coatings, as the initiator can change their shade and reduce fastness properties. Reputable pigment manufacturers publish data on such systems and can usually help in case of difficulties.

The second possible attack can come from chemicals with which the coating comes into contact. Water, in the form of condensation, can seriously affect a paint film, including domestic situations such as bathrooms and kitchens. Many of the detergents used for cleaning paintwork are harsh and aggressive towards the pigment. If the coating is to come into contact with food it is essential that not only the coating is unaffected, but the food must also remain completely unchanged. Before one dismisses the possibility of food affecting a paint film, remember how many foods contain acid (vinegar), alcohol, and fatty acids.

Most test methods associated with chemical stability consist of applying the chemical to the surface of the coating, keeping them in contact for a given time, then measuring the discoloration of the coating and/or the staining of the chemical concerned. By the very nature of the wide demands made on a coating, published data will be of limited value; therefore it may be necessary to devise special tests to reproduce conditions found in practice.

3.3.10 Heat stability

Few pigments degrade at temperatures normally associated with coatings. However, several pigments will change shade because they become more soluble as the temperature is increased. Therefore for organic pigments, heat stability is closely related to solvent fastness. Nevertheless, pigments that may prove entirely satisfactory at one stoving temperature may prove quite unsatisfactory at an application requiring a 10°C higher stoving temperature.

Chemical stability is also more likely to be critical at elevated temperatures; this is often very relevant in powder coating systems. Another critical area is in coil coatings, where metal complex pigments may react with stabilizers at elevated temperatures, producing distinct changes in shade. Elevated temperatures can also result in a modification in the crystal structure of pigments.

Pigments with a highly crystalline structure are usually more heat stable than polymorphic pigments, where the different crystal modifications may respond differently to heat. Generally, inorganic pigments have superior heat stability, but

an exception is yellow iron oxide, which loses water from the crystal at elevated temperatures.

Heat stability must always be regarded as system dependent and this must be reflected in any tests. All tests work on the principle of assessing the colour at a series of different temperatures and measuring the colour difference between the sample in question and a standard that has been processed at the minimum temperature.

3.4 Pigment classification

Trying to place all pigments into a logical and meaningful classification system is not really possible. This is especially true for pigments that are not primarily used for their colour, such as white and extender pigments. Coloured pigments have traditionally been classified as either organic or inorganic. While there are characteristics associated with each of these two classes of pigment, modern manufacturing techniques are developing new products, which impart properties not previously associated with their chemical type, e.g. organic pigments have traditionally been transparent; however, there are now organic pigments with high opacity.

Inorganic pigments have a long history, going back to the early cave paintings that are about 30000 years old. They can occur naturally, but for the manufacture of paint they usually need refining. However, they are increasingly synthesized. All the white pigments are inorganic as are a broad range of coloured pigments.

Organic pigments are relatively new. Although natural dyes have been precipitated on to inorganic bases (known as lakes) and used in artists' colours since the middle ages (e.g. madder lake and crimson lake), true organic pigments have only been known since the early years of the twentieth century. They are derived from fossil fuels, usually oil.

The properties that have traditionally been associated with inorganic and organic pigments are summarized in Table 3.2. A more detailed classification of inorganic and organic pigments into chemical types is shown in Fig. 3.2 and typical properties associated with chemical types are shown in Table 3.3.

Table 3.2 — Traditional properties associated with organic and inorganic pigments

Pigment property	Inorganic	Organic
Colour	Often dull	Usually bright
Opacity	Normally high	Normally transparent
Colour strength	Usually low	Normally high
Fastness to solvents — bleed resistance	Good	Varies widely from good to poor
Resistance to chemicals	Varies	Varies
Heat resistance	Mostly good	Varies
Durability	Usually good	Varies
Price	Often inexpensive	Varies, but some are expensive

Table 3.3 — General properties of pigment chemical types

Properties in paint	Titanium dioxide (coated)	Iron oxide (not <i>trans</i>)	Prussian blue	Lead chromate	Carbon black	Monoazo	Disazo	Disazo condensation	Metal azo toner	Phthalo- cyanine
Colour	E	F	E	E	E	E	E	E	E	E
Opacity	E	E	E	E	E	F–G	F–G	F–G	F–G	P
Tinting strength	E	P–F	G	F	E	G–E	E	F–G	G–E	E
Heat stability	E	G–E	G	G	G	P–F	G	E	G	E
Fastness to solvents	E	E	E	E	E	P–F	G	E	G	E
Resistance to										
Acids	E	E	F	F–G	E	E	E	E	P	E
Alkalis	E	E	P	P	E	E	E	E	P	E
Chemicals	E	E	P	G	E	E	E	E	P	E
Light fastness										
Full/near full shades	E	E	G	G	E	G–E	F–G	E	F–G	E
Pale reductions	E	E	F	P	E	F	P–F	F–G	P–F	E
Dispersibility	E	E	F	G	F–G	G	G	G	G	F
Flow properties	E	E	G	E	F	G	F	G	F	P
Flocculation resistance	G	G	G	E	P	G	G	G	G	F
Price	Low	Low	Low	Low	Low	Low– high	Low– medium	Medium– high	Low– medium	Low– Medium

E, excellent; G, good; F, fair; P, poor (however, within most categories there can be notable exceptions).

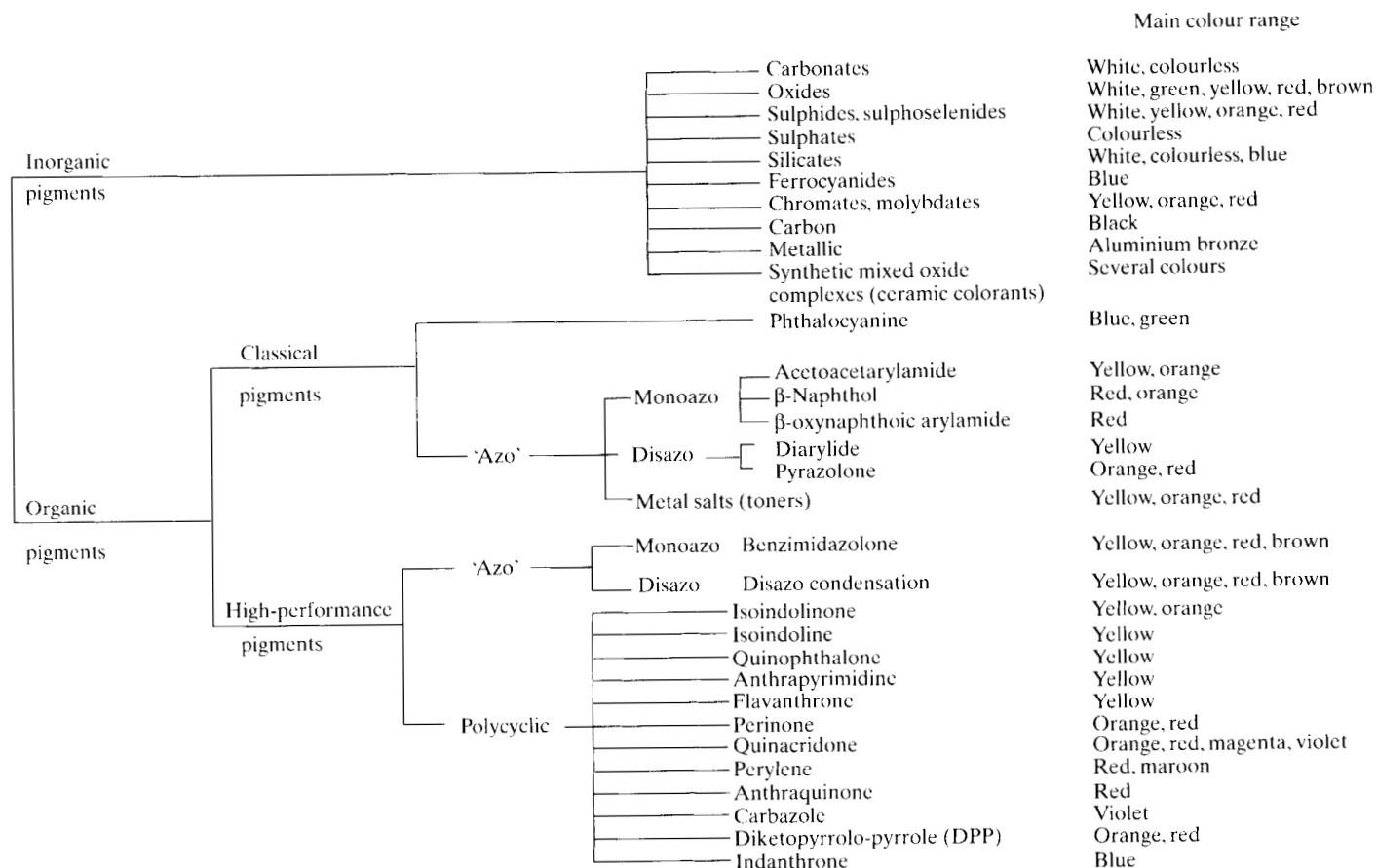


Fig. 3.2 — Pigments for paint, white, coloured and extenders (classification by chemical type).

3.5 **Pigment nomenclature**

Although a number of pigments are known by their common names, sometimes associated with their chemical type (e.g. toluidine red), connections with their origin (e.g. Prussian blue), or their original trade name (e.g. Hansa® Yellow), the most common system used for identifying pigments are Colour Index (CI) names and numbers.

The *Colour Index International* [11] provides a logical and comprehensive way of identifying the essential chemical nature of dyes, pigments, intermediates and optical brightening agents. However, there is also a *Pigment and Solvent Dyes* version [12]. This only lists pigments and solvent soluble dyes.

Colorants are designated by a generic name, e.g. CI Pigment Yellow 3. This generic name is used for all pigments (or dyes) that have an identical chemical structure. The chemical structure, where known, is indicated by the five-figure *constitution number*, e.g. 11710. The chemical class to which the colour belongs (e.g. monoazo) and the hue (e.g. bright greenish yellow) are given.

The third edition has three main sections:

- 1 Tables indicate the pigments' physical properties, such as solvent fastness and light fastness. However, this can be misleading as products designated CI Pigment Yellow 3 do not necessarily have identical application properties. Particle size distribution, surface treatments, and method of manufacture can all have a pronounced effect on the pigment's colour, colour strength and fastness properties. Therefore, pigments registered under such a generic name while chemically identical may not necessarily have the same physical properties.
Separate sections of the complete *Colour Index International* list dyes by application categories, e.g. CI Acid Blue 1, CI Vat Orange 7.
- 2 The chemical constitution, where published is shown in order of their CI constitution number. An indication of the method of synthesis, the name of the first known maker and references are often given where these are known. There are a few products that have not been allocated a constitution number, as the constitution has not been disclosed.
- 3 This section is split into three sub-sections. The first section lists the names, addresses, and code letters attributed to colorant manufacturers. The second

Table 3.4 — Number and chemical types of pigments listed in the 1997 *Colour Index*

<i>Colour Index</i> pigment	No. of different chemical types listed
White	15
Black	24
Brown	23
Blue	36
Green	19
Yellow	122
Orange	36
Red	146
Violet	26
Metal	3

Table 3.5 — Main pigments by volume

Pigment	Type
CI Pigment White 6	Titanium dioxide
CI Pigment Red 101	Red iron oxide
CI Pigment Yellow 42	Yellow iron oxide
CI Pigment Blue 15, 15:1, 15:2, 15:3, 15:4	Copper phthalocyanine
CI Pigment Yellow 13	Diarylide yellow (AAMX type)
CI Pigment Red 57:1	Monoazo 'Lithol® Rubine' toner

section lists all the colorants in order of generic name and lists all the commercial names that have been registered as being that generic name with the manufacturer's code. Finally the commercial names of all registered products are given with their appropriate manufacturer's code, generic name and constitution number.

The complete *Colour Index International*, is now available in the form of a CD-ROM. The 'Pigment and Solvent Dye' edition [12] is simpler to use, as it combines the chemical structure and associated information with all the commercial names of products with that structure. The main application is listed and there is an opportunity for manufacturers to distinguish their commercial product. A second section lists commercial products under their trade name, giving their CI name and constitution number. A breakdown of the entries in this edition is given in Table 3.5. This is also available in a CD-ROM format.

Of all these pigments, excluding extenders, about 30 account for 80% volume of the total manufacture and consumption. In Table 3.5 some of these main pigments are listed. It should be noted that in the case of the coloured pigments, the influence of the printing ink industry, which has a higher consumption of coloured pigment than the paint industry, predominates.

3.6 Further types of pigments and terms used

3.6.1 Inorganic pigments

The most important pigment in coatings is without doubt titanium dioxide — or more correctly titanium (IV) oxide. It combines a pure white colour with a high refractive index, making it opaque. Efforts to improve its surface have resulted in pigments that are easy to disperse. Early grades were prone to a defect known as chalking. This was caused by a photochemical reaction in which radicals broke down the binder, leaving a chalky effect on the surface of paints, owing to particles of pigment becoming exposed on the surface. This reduces the gloss of the finish and in the case of coloured finishes gives a whitening effect on the surface that develops over a period of time. However, surface treatment of the pigment can now minimize this effect.

Titanium dioxide is now universally used as the white pigment in paint, but like many organic pigments it exists in more than one crystal modification [13]. Brookite is not used as a pigment. The anatase grade is a slightly bluer white and is softer in texture. However, it has two major disadvantages. It is far more likely to chalk than the rutile crystal form and it has a lower refractive index (2.55) and is therefore less

opaque than the rutile grade (refractive index of 2.76). Consequently, for surface coatings the rutile grade is usually preferred.

If we trap a foreign ion into the rutile crystal lattice, we can obtain some weakly coloured pigments that are known as mixed metal oxides, or less correctly as 'titanates'. Such pigments were developed for the ceramic industry, but are now used for either pale shades with excellent fastness properties or in place of titanium dioxide in near full shades. Nickel (greenish yellow) and chromium (reddish yellows) ions are the most commonly used to obtain such pigments.

3.6.2 Types of organic pigment

Many of the organic pigments we now use derive from dyes that were developed for the textile industry. In Table 3.5, the last pigment is described as a 'toner'. This term can be confusing because it has different meanings in different countries. Another term that causes confusion is 'lake', again because usage varies in different parts of the world. In this chapter we will adopt the UK usage, as it is the most precise [11].

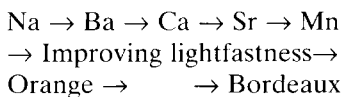
In the USA the term 'toner' is used to describe all organic pigments, as they are used to 'tone' duller inorganic pigments, whereas the term 'lake' is used to describe both lakes and toners in UK usage.

3.6.2.1 Pigment toners

Toners are essentially metal salts of dyes, mainly acid dyes, in which the anion is the source of the colour. Most acid dyes are lithium, potassium, sodium, or ammonium salts. However, salts produced with metals such as calcium, manganese, barium, and strontium are mainly insoluble. Therefore, this is an easy method of producing relatively simple and economic pigments that find significant usage, especially in printing inks.

CI Pigment Red 57:1 (Lithol® Rubine or Rubine toner), which is normally used as the standard magenta in three and four colour printing processes, is the most important pigment of this type. CI Pigment Red 53:1 (Lake Red C — which in spite of its name is in fact a toner) and CI Pigment Red 49:1 (Lithol® Red) are the most important in inks. CI Pigment Red 48:4 (2B toner) is frequently used in industrial paints. However, this method of producing insolubility in the molecule is now being increasingly adopted in the development of pigments for plastics, where much more complex anions are being utilized, providing toners with a significantly better light fastness. CI Pigment Yellow 183, Pigment Yellow 191 and Pigment Red 257 are good examples.

The metal ion used for the toner does have an influence on both the colour and the fastness properties of the pigment:



It is also possible to produce salts from basic dyes, in which it is the cation that produces the colour, but this is a little more difficult. Cationic dyes (or basic dyes) are usually in the form of quarternary ammonium salts, so in order to make the molecule insoluble one has to use complex acids, producing phosphomolybdate, phosphotungstomolybdate, phosphotungstate, silicomolybdate, or ferrocyanide complexes. These pigments are often known as Fanal® pigments. Their use is mainly

limited to printing inks, usually for packaging. They have intense, very bright colours, but limited fastness properties especially to light and chemicals.

3.6.2.2 Lakes

The first lakes were natural dyes which were then absorbed on to an absorbent inorganic base such as blanc fixe or alumina hydrate. Following the discovery of the first synthetic dye by Perkin in 1856 and subsequent discoveries, countless new dyes became available and many of these could be similarly precipitated. Such lakes are rarely used today except occasionally in inks and food dyes (tartrazine lake, etc.). Some of the last to survive are quinizarin lake (CI Pigment Violet 5), which uses alumina as a base, and pigment scarlet 3B lake (CI Pigment Red 6O:1), which uses aluminium hydroxide and zinc oxide as a base.

Just in case anyone is tempted to feel the need to go back to nature, beware! The consequences of producing lakes from natural dyes appear to have had a much more damaging impact on the environment than current manufacturing methods. In the Middle Ages the production of blue dyes and lakes from woad was severely curtailed because of the catastrophic effect it was having on the environment. The woad plant requires large quantities of potassium, so the soil on which it was cultivated quickly became devoid of the mineral and thus completely infertile. Another step in the production process involves fermentation, during which obnoxious gases are given off, making life intolerable for those living within 3 km (two miles). Finally, the waste produced contaminated watercourses, reeking havoc on town and countryside alike.

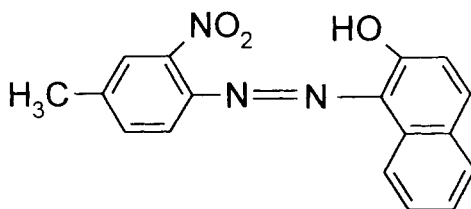
To reiterate, the term 'lake' is widely used in the USA and elsewhere to describe what are known as 'toners' in the UK.

3.6.2.3 Organic pigments

Organic molecules that are insoluble, without having to precipitate on to a base or being made insoluble by conversion into a salt, used to be called pigment dyestuffs. However, this confusing term is no longer encouraged. The term 'organic pigment' will suffice. They can be conveniently sub-divided into two, azo pigments and polycyclics.

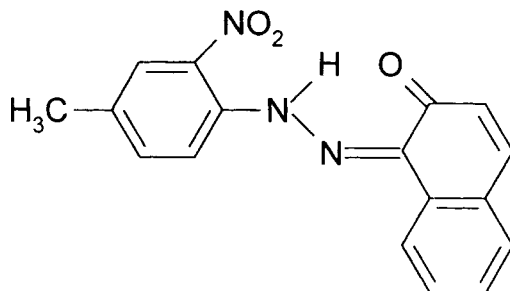
3.6.3 Azo pigments

This is by far the most important sector and includes about 70% of all organic pigments, especially in the yellow, orange, and red parts of the spectrum. As well as including many pure organic pigments, the azo types also include many of the toners. The traditional structure has always been assumed to be the azo structure, characterized by the —N=N— group, e.g. CI Pigment Red 3 has always been designated by its assumed constitution based on an azo structure:



Traditional structure assigned to CI Pigment Red 3

However, work [14] on the measurement of bond lengths and bond angles convincingly shows that this pigment does not actually contain the azo group, but has a hydrazone structure. This would allow a more planar structure and in part explains the insolubility of the molecule. CI Pigment Red 3 is now considered to have a hydrazone structure:



More recent structure assigned to CI Pigment Red 3

Many other pigment structures have been investigated and the evidence suggests that all had the hydrazone, rather than the previously assumed azo structures [15, 16]. While the term 'azo' is unlikely to be changed, like the *Colour Index* we will adopt the 'hydrazone' structure, as the evidence that this is the correct structure is very convincing.

Azo pigments can be subdivided into monoazo and disazo pigments.

3.6.3.1 Monoazo pigments

Monoazo pigments have the simpler structure and tend to have poorer solvent stability. The simplest types are the β -naphthol pigments represented by CI Pigment Red 3 (toluidine red). In the yellow part of the spectrum the simplest pigments are the arylamide yellow pigments, such as CI Pigment Yellow 1. These pigments (with the exception of CI Pigment Yellow 97 — see section 3.12.4) can only be used for water-based media or for media that are soluble in weak organic solvents such as white spirits. They have poor heat stability, whereas light fastness varies from poor to very good.

β -Naphthol colorants are among the oldest synthetic colours still being manufactured. They owe their origin to the textile industry, being introduced in 1880 as 'developing dyes'. Cotton impregnated with β -naphthol (2-naphthol) and dried, is then passed through a liquor of ice-cold diazonium compound, forming a coloured pigment inside the fibre. Five years later, Gallois and Ullrich produced para red (CI Pigment Red 1) in its own right and it can therefore be considered the first true synthetic organic pigment. Although para red is rarely used today, several pigments with a similar structure are still important, especially for decorative paints.

More complex are the *arylamide red* pigments (also known as *BON arylamides* from their chemical basis—Beta Oxy Naphthoic acid, or *naphthol AS*® pigments). They have an additional benzene ring attached to the β -naphthol by a carbonamide linkage (—CONH—). The higher molecular weight and this carbonamide linkage

improve the solvent resistance of these pigments. The extra benzene ring also provides more sites for additional substituents, thus extending the colour range from orange through to violet and allows the possibility of improving solvent resistance even further. Consequently, these pigments have a wide range of properties from moderate to very good.

Solvent fastness can be increased even further by the addition of the carbonamide group in a cyclical form. This replaces a benzene ring with 5-aminocarbonyl benzimidazolone, giving rise to the name given to such pigments — *benzimidazolone*. The range of colours goes from very green shade yellow, through orange, red right through to violet. They have good to excellent solvent fastness and good to excellent light fastness.

3.6.3.2 Disazo pigments

Disazo pigments can be divided into two groups. The *diarylide* pigments form the larger and older group. They are mostly based on 3,3'-dichlorobenzidine, but their low light fastness means they find most use in the printing ink industry. Nevertheless, their high colour strength and good resistance to solvents and heat does mean they can be used for some industrial paint applications. Of particular interest is the opaque form of CI Pigment Yellow 83 on account of its superior light fastness and can therefore be used for more demanding applications. The colour range can be extended into the orange and even red part of the spectrum by using aryl-substituted pyrazolones.

The other group contains the high-performance *disazo condensation* pigments, that consist of two monoazo pigment molecules containing an acid group joined together by condensing with a diamine. The higher molecular weight thus obtained, plus the two carbonamide groups formed by the condensation reaction, give such molecules very high resistance to solvents and heat, coupled with good light fastness. The range of colours obtained goes all through the spectrum from greenish yellow to bluish shade red and also includes brown.

3.6.4 Polycyclic pigments

This is a convenient term used to link most of the organic pigments that are not classified as azo. They are defined as compounds with more than one five or six-membered ring in their chemical structure. Many of the pigments in this category were originally developed as vat dyes. They only came into consideration as pigments when work in the USA modified their surface by a process called conditioning, allowing the products to be dispersed into a fine particle size. They are expensive to manufacture and can only be economically justified where their good heat stability chemical and solvent resistance and good durability, even in pale shades, are needed. A few of these pigments do have a tendency to darken on exposure to light, especially when used in higher concentrations.

Within this classification are also included *phthalocyanine* pigments, which are of such importance they constitute a group in their own right, having various crystal forms and substituted derivatives. A number of other polycyclic pigments have been developed. *Quinacridone* pigments also exist in two crystal forms and include various substituted grades, the best known of which is quinacridone magenta (CI Pigment Red 122). *Dioxazine violets* are most useful pigments, allowing one to redden off blue and blue off reds without losing brightness.

In many ways *isoindolinone* pigments can be considered to be the ultimate in chemical ‘architecture’. The molecule contains two —CONH— groups and all the spare sites on the outside benzene rings are chlorinated. As one could predict, these pigments have excellent fastness to light and excellent solvent fastness, but have relatively low colour strength. A simpler pigment, with slightly lower fastness but higher colour strength is *isoindoline* (CI Pigment Yellow 139).

An important group of pigments for high-quality coatings are the *perylene*s, which range from a mid red (CI Pigment Red 149) through a bluish red grade (CI Pigment Red 224) to black (CI Pigment Black 31 and Black 32). Some of these pigments are available in high-opacity grades, ideal for full shades, or in high strength, transparent grades that are used for metallics.

In the yellow/orange part of the spectrum there have been a number of metal complex pigments based on *azomethine*. These pigments give very interesting effects when used in metallic finishes but are less interesting for solid shades as they are rather dull.

A significant new group of pigments has been the *diketopyrrolo-pyrrole* (or DPP) which combine high fastness properties with a wide range of shades. Again they lend themselves to careful selection of particle size, so the same chemical pigment may be in more than one form, one having high opacity and the other high strength and transparency. They are mainly used in automotive and other high-fastness demand finishes.

3.7 Particulate nature of pigments and the dispersion process

3.7.1 Crystal structure

Pigments can be crystalline or non-crystalline (i.e. amorphous). For pigments to be crystalline, the atoms within each molecule are arranged in an orderly fashion, but in amorphous pigments the atoms are random. Some materials are capable of existing in several different crystalline forms, a phenomenon called polymorphism.

Application properties, not least colour, are not only dependent on the chemical constitution but also on these different structures. Certain pigments may have chemically identical entities in different crystal forms, which are not suitable for use as a pigment. Examples of polymorphic pigments include titanium dioxide, phthalocyanine blue and linear trans quinacridone.

Pigment manufacturers are developing techniques that influence the formation of a desired crystal form and particle size distribution, in order to optimize the commercial product for end applications.

3.7.2 Particle shape

The shape of a pigment particle is determined by its chemical structure, its crystalline structure (or lack of it) or how the pigment is synthesized. The primary particles of a pigment may be:

- Spherical — unlikely in practice;
- Nodular — irregular shaped;

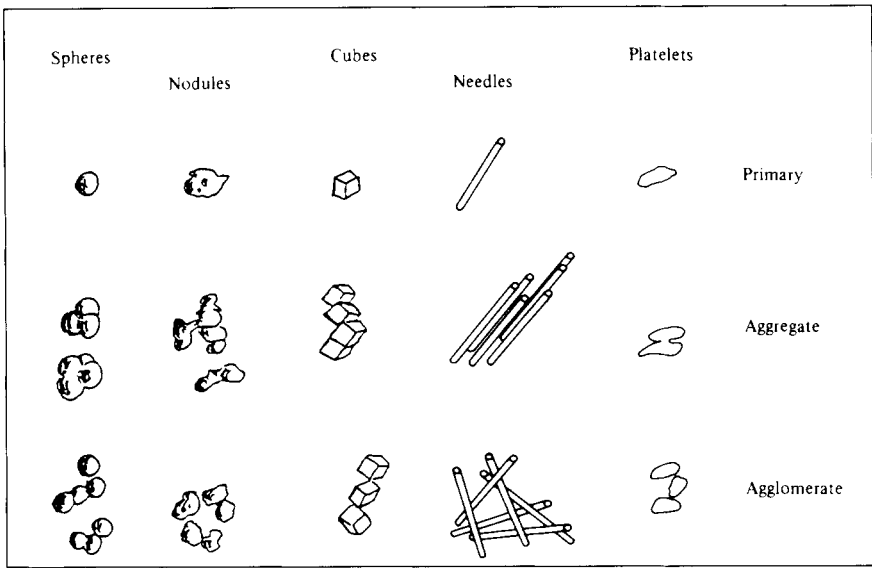


Fig. 3.3 — Particle shapes.

- Prismatic — cubic;
- Acicular — needle-like;
- Lamellar — plate-like.

These shapes are illustrated in Fig. 3.3.

Primary particles consist of single particles. The smaller these particles, the greater their surface energy and therefore there is an increased tendency to clump together during the manufacturing process. However, even if it were possible to supply pigments in the form of primary particles, it would be quite impractical, as they would be more like smoke than a powder. In practice, they only exist as the pigment is synthesized. When the particles clump together during the manufacturing process they form either aggregates or agglomerates.

Aggregates are joined along crystal boundaries during synthesis or drying. They are difficult to separate and therefore the pigment manufacturer tries to avoid their formation during the pigment's production.

Agglomerates are loose clusters of primary particles, and can be broken down by efficient dispersion processes.

The states of aggregation and agglomeration are key factors in the pigment's dispersibility. Once dispersed it is still possible for particles to re-agglomerate, into loosely held groups, known as flocculates. It frequently occurs when there is a rapid change of state, such as too rapid a dilution, or the addition of an incompatible substance. Flocculation results in a loss of tinctorial strength. However, flocculates are usually easier to separate than true agglomerates, and even normal shear such as brushing out is sufficient. This results in an uneven increase in tinctorial strength, depending on how much shear has been developed during brushing out. Small particles are more prone to flocculation than larger ones, so pigments most at risk are grades of carbon black and conventional fine organic pigments, such as phthal-

cyanine and dioxazine violet pigments. However, there are an increasing number of flocculation-stable grades coming on the market.

The crystal shape of a pigment, particularly in the case of larger particles, does influence the way they pack in the paint film and consequently can affect the properties of the paint. Thus, properly dispersed acicular particles are said to reinforce the paint film like the fibres in glass fibre reinforced plastics. Lamellar particles such as aluminium and mica, form an overlapping laminar structure, not unlike roof tiles, and like roof tiles they offer resistance to the passage of water, allowing the paint film to impart good protection properties to the substrate.

Particle shape can also influence the shade of a pigment. It has been shown that β -copper phthalocyanines (CI Pigment Blue 15:3) give different hues, depending on the deviation from isometry to acicularity [17].

3.7.3 Particle size and particle size distribution

It is important to distinguish between the particle size distribution of the powder pigment and that of a pigment dispersed in the binder system. Particle size is normally expressed as an average diameter of the predominant primary particles. However, pigment particles are not usually spherical, and therefore may have different dimensions depending on whether one measures the length, width or height. This requires making a number of assumptions and simplifications. Typical ranges are:

- carbon black — 0.01 to 0.08 μm ;
- organics — 0.01 to 1.00 μm ;
- inorganics — 0.10 to 5.00 μm ;
- titanium dioxide — 0.22 to 0.24 μm .

Extender pigments can be among the coarsest pigment particles, up to 50 μm , but other types can be exceptionally fine (e.g. the precipitated silicas).

The particle size of small particles is difficult to measure, and is made even more difficult by the fact that one needs a dilute suspension, and dilution can often result in flocculation, thus changing the size of the particles. Sedimentation methods were employed [18] but increasingly techniques involving the use of lasers are employed [19].

3.7.4 Surface area

Although measuring the surface area does not give any information about the shape of crystals, it is still most useful as it is closely linked to the pigment's demand for binder. It is usually defined in terms of the surface area of 1 gram of pigment and has the unit of square metre (m^2). Typical values for organic pigments are between 10 and 130 m^2 . Most manufacturers give the surface area of their pigments in technical literature. Measurement is usually made by calculating the adsorption properties of the pigment, using the Brunauer, Emmett, and Teller (BET) equation with either nitrogen or argon as the gas [20].

Larger particles have a smaller surface area and therefore a lower demand for binder. Measurement of the surface area has largely replaced the former measurement 'oil absorption' which tended to be too subjective. A pigment's oil absorption

is expressed as the weight of an acid-refined linseed oil in grams, required to produce a smooth paste with 100 grams of pigment. Even with standard oils the method is dependent on how the test procedure is conducted, but can give useful advice on formulating efficient mill bases for the dispersion process. The ease with which a pigment can be wetted out also influences the oil absorption.

Care must be taken when using heavily surface-treated pigments, as these can give very strange results, but such pigments are not widely used in the paint industry.

3.7.5 Dispersion

Efficient and effective pigment dispersion is necessary in order to obtain optimum tinctorial strength, cleanliness of shade and good gloss from the final coating. Most organic pigments also show better transparency as dispersion improves, while in the case of the larger particle size inorganic pigments, opacity is improved by good dispersion.

The dispersion process consists of the permanent breaking down of agglomerates into, as far as possible, primary particles. The smaller the primary particle, the more difficult this process becomes, although the finishing treatments given to the pigment, including the addition of surface-active agents, can bring about tremendous improvements. Consequently, organic pigments tend to require more dispersion than inorganic pigments. It is possible to overdisperse some pigments, especially those with needle-like crystals, such as bluish red iron oxides, and inorganic pigments which have a protective coating, such as molybdate red. If this coating is worn down, the fastness properties of the pigment can be significantly reduced. Although the process is often described as 'grinding', this is rarely accurate. There are four aspects to the dispersion process, which can to some extent take place alongside one another.

- 1 *Deagglomeration* is the breaking down of the agglomerates by the shear forces of the equipment being employed. A mixture of crushing action and mechanical shearing force provides the means of breaking down agglomerates. A higher viscosity leads to greater shearing forces, but the specific equipment being used will put practical limits on the viscosity of the millbase.
- 2 *Wetting out* takes place at the pigment surface and requires a binder or surface active agent to anchor itself on to the pigment's surface and act as a bridge between the pigment and the binder itself. The wetting process can be calculated [4, p. 77]. The calculation reveals that the time to wet out is directly proportional to the viscosity. The heat generated by the mechanical shearing process results in an increase in the temperature of the mixture, thus assisting in the wetting out process. However, this temperature rise also reduces the viscosity, thus reducing the effectiveness of deagglomeration, a phenomenon supported by experience and research [21].
- 3 *Distribution* requires the pigment to be evenly spread out throughout the binder system. It tends to be favoured by a lower viscosity.
- 4 *Stabilization* prevents the pigments from re-agglomerating. It is often neglected in the manufacturing process. While the theories that try to explain stabilization are complex, in practice it is found that it is during the dilution process that prob-

lems are most likely to occur. These problems can be minimized by diluting as slowly as possible, so that the pigment can be stabilized at each stage before further dilution takes place.

3.7.6 Dispersion equipment

The choice of dispersion equipment must be made with the end application clearly in mind. One of the most effective machines for dispersion is the three-roll mill, which can deal with high-viscosity systems and coarse pigments. However, it is rather slow and labour intensive. On the other hand, ball mills require very little labour, but are not very effective when dealing with coarse pigments and higher viscosity systems. Between these two pieces of equipment there have been some very significant developments based on sand and bead mills. Every machine has its own specific requirements and therefore the experience of those employed to run them efficiently must be considered [22].

No matter how proficient modern mills are, all operate more efficiently when used with a good premix prior to passing through the mill. An effective premix should contain sufficient wetting agent or binder to coat the pigment particles. However, it must also be of low enough viscosity to produce a millbase that will proceed through the mill. It must be remembered that the dispersion process itself will inevitable increase viscosity as binder is absorbed by the new pigment surfaces that are produced, owing to the resultant increased dispersed particle phase volume. This effect may, however, be counteracted by the viscosity decrease resulting from the temperature increase during the milling process.

The beads (or sand) in the mill also play an important role. The nearer to a perfect sphere the better, hence Ottawa sand is considered to be the best natural milling material. The higher the density of the beads, the better the dispersion that can be achieved. Glass beads are frequently used but steatite, zirconium oxide, and the more resistant to wear zirconium silicate are more dense and therefore have advantages. In spite of its price, even yttrium-stabilized zirconium beads provide a higher density and greater hardness. However, it is important to ensure the beads used are suitable for the mills being employed as they may result in wearing out the lining of the mill's chamber. Economics can also play an important role, some of the more expensive beads such as the yttrium-stabilized zirconia are reputed to wear out at a much slower rate and retain their spherical shape. They may also remain much smoother, thus producing less heat and wear on the impeller discs and the chamber walls.

While smaller beads can also improve dispersion, when mixed with the millbase these smaller beads will result in a higher viscosity that can strain or even block the mill. The less dense the milling media, the more critical this effect, so it is possible to use smaller steatite beads than glass under the same conditions. The technology of separating beads from the millbase is constantly developing and seals and screens are now much more efficient and open up new options.

The dispersion process is accompanied by an increase in temperature of the millbase. This can be very significant and some pigments will be adversely affected, especially pigments with poor resistance to solvents. The pigments can dissolve, leading to recrystallization and subsequent colour strength and shade stability problems. Therefore, when dispersing such pigments it is important to ensure there is sufficient mill cooling to prevent the millbase becoming too hot, by using as cold a chilling

medium as possible and by having a sufficient cooling surface area to millbase volume. Note that as mills increase in size, the ratio of surface area to volume reduces proportionally to the diameter.

3.8 Manufacture of pigments

Many of the inorganic pigments can be obtained from natural sources, but paint industry's demand for consistency mean that even these natural pigments, such as iron oxides, are now being made synthetically. The main pigments used in their natural form are the so-called extenders, which include china clay, barytes, and chalk. Commercial organic pigments are all made synthetically, originally from coal tar but now from petroleum distillates.

3.8.1 Synthetic inorganic pigments

Each group of inorganic pigments has its own manufacturing route. Some are the result of simple chemical reactions, such as lead chromates and molybdates. Chrome yellow (CI Pigment Yellow 34) can be manufactured by mixing solutions of lead nitrate with sodium chromate.

Other inorganic pigments such as titanium dioxide (CI Pigment White 6) depend on the extraction of the desired compound from ores, either from ilmenite (FeTiO_3) by the sulphate process or from rutile (impure TiO_2) by the chloride process.

In recent years the chloride route has developed, as it lends itself to continuous production, produces a slightly purer white, and has advantages with respect to environmental concerns. The rutile ore is treated with chlorine in the presence of coke at a temperature of around 800–1000°C. Titanium tetrachloride gas is formed. It is condensed and purified by fractional distillation. The purified titanium tetrachloride is then superheated and passed into a reaction chamber with oxygen at about 1500°C. After cooling the reaction products are separated and the chlorine gas recycled [23].

Ultramarine blue, which is a synthetic version of the semiprecious mineral lapis lazuli, can be manufactured by the calcination of china clay, silica, sulphur, and a carbonaceous material such as coal tar pitch. Temperatures of around 800°C for two to four days are required, followed by cooling in an oxidising atmosphere for several days. For other pigments, calcination can sometimes be used to change or modify the crystal structure.

Iron oxide pigments do occur naturally, but for the paint industry synthetic grades predominate. They cover a wide area of the spectrum from yellow ochre (CI Pigment Yellow 42), through red ochre (CI Pigment Red 101), brown (CI Pigment Brown 6) to black (CI Pigment Black 11). They are manufactured by various methods [24].

Carbon black (CI Pigment Black 7) is made by the partial combustion of natural gas. The process most frequently used is the furnace process [25].

Following any synthesis, pigments have to be washed, filtered, dried, milled, and finally classified. Additives to improve the manufacturing procedures and also to modify the final pigment properties are included at various stages of the production process.

3.8.2 Synthetic organic pigments

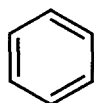
The synthesis of organic pigments from oil is a multistage process involving many critical steps. In the case of some of the more complex pigments, which can involve over 20 syntheses, it may take many months, and until the final step one is never sure that the process has been satisfactory.

The pigment manufacturers are unlikely to carry out all these steps themselves, so that materials from each stage may be sold between manufacturers to achieve such benefits as cost savings derived from economies of scale and greater utilization of specialist plant.

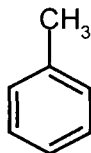
The materials at each stage are given the terms:

- 1 primaries;
- 2 substituted primaries;
- 3 intermediates;
- 4 crude.

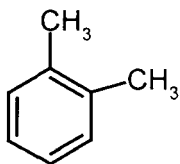
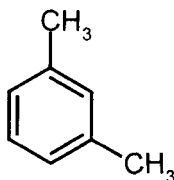
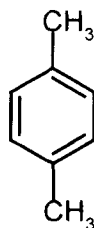
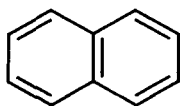
Primaries are obtained directly from petroleum distillation. The most important are the aromatic hydrocarbons:



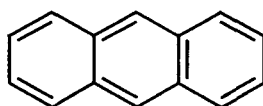
Benzene



Toluene

*Ortho-xylene**Meta-xylene**Para-xylene*

Naphthalene



Anthracene

These primaries are converted into 'substituted primaries' and then into intermediates by a variety of well-known classical chemical reactions. Hundreds of

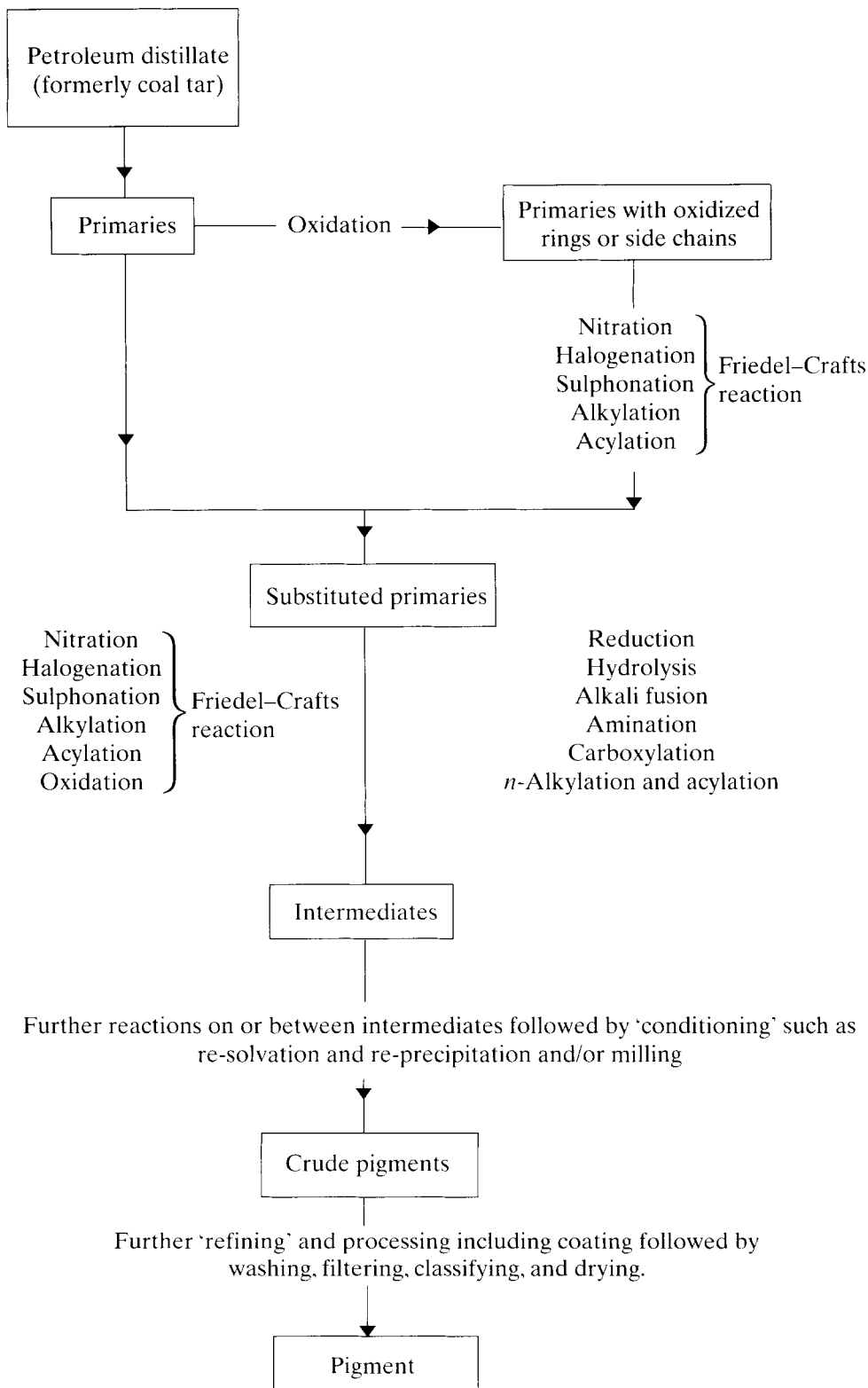


Fig. 3.4 — Typical production processes for organic pigments.

intermediates are involved. Some may be manufactured as specialist products from one or two manufacturers; others may be commodity type products bought on the open market.

A schematic production process is shown in Fig. 3.4.

As typical examples of pigment manufacture we will look at two very important classes of pigment. Since around 80% of all organic pigments are classified as azo pigments we will use the preparation of toluidine red (CI Pigment Red 3) as typical to illustrate a simple azo process:

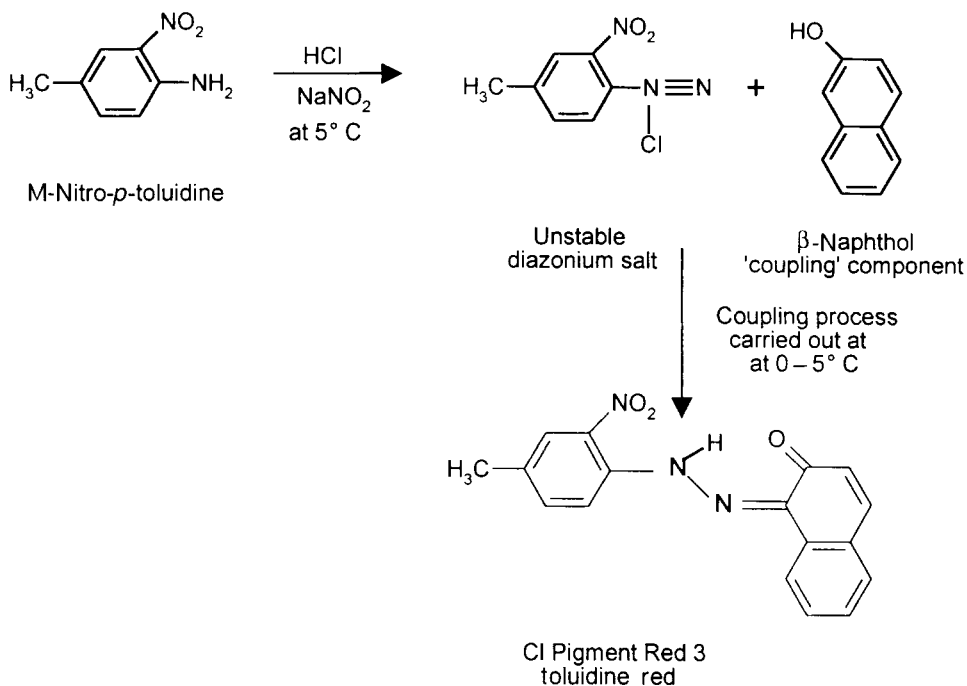
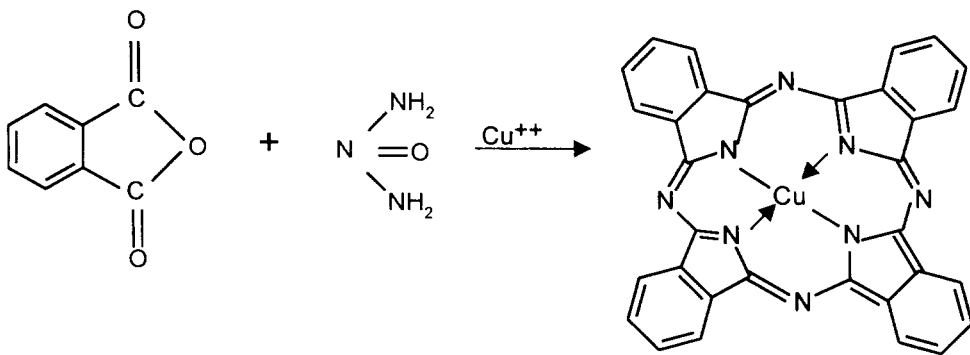


Fig. 3.5 — Production of typical azo pigment, toluidine red.

There are several methods of manufacturing copper phthalocyanine, but two predominate. The most frequently used and the cheaper route starts from phthalic anhydride and urea and has been used in the UK and the USA. It takes place in either an organic solvent or in the vapour phase. The vapour phase is becoming more popular as it produces less undesirable by-products. Phthalic anhydride is melted with urea above 150°C in a rotating drum in the presence of a catalyst. A copper salt, such as copper (II) chloride is added and the temperature increased to about 200°C . The reaction mixture is cooled, washed and steam distilled to remove impurities. The resulting product is known as crude copper phthalocyanine and is of little use unless further processed. Some pigment manufacturers produce their own 'crude' while others purchase the crude and condition themselves.



Production of a phthalocyanine pigment from phthalic anhydride

However, a technically superior product can be obtained from phthalonitrile, using a process developed in Europe and traditionally favoured by German manufacturers.

3.8.3 Pigment conditioning

The chemical synthesis of both organic and inorganic pigments is by no means the final stage. The chemical compound formed has to go through further processing before becoming a commercial product, and it is often these stages that allow the experienced pigment manufacturer to offer commercial products that have application advantages. These stages usually include many washings, filtering, drying, and classification.

For a typical *azo* pigment, synthesis would result in the formation of tiny insoluble particles (primary particles). The manufacturing conditions such as temperature, pH, and rates of addition will all influence the crystal shape and crystal size of the product. The solid particles have to be separated from the liquor by filtration, which is achieved by means of a filter press. The slurry is squeezed under intense hydraulic pressure, which results in the so-called 'presscake'. Normal presscakes would contain about 30% pigment, but modern equipment can achieve over 50% pigment. This looks like a damp powder. The drying process results in the primary particles joining together to form agglomerates and aggregates. Agglomerates are loose associates of primary particles and can be broken down by the dispersion process, whereas aggregates are joined along crystal boundaries. The resulting hard-grained pigment is virtually impossible to disperse, so if it were used in paint the paint would develop poor colour strength.

Even if one could obtain pigments in the form of primary particles, it would be quite impractical. They are so small and light that they would resemble smoke. However, by careful control of the conditions and after treatment one can develop optimum application properties. The first stage is to wash out the salts and impurities from the presscake with water. Various methods are then used, but traditionally heating the purified pigment suspension in water removes some of the very fine particles that are mainly responsible for forming harder agglomerates. In the case of the more complex pigments with lower solubility, it is necessary to use solvents

or solvent/water mixtures at elevated temperatures. This treatment has become very well developed. In addition certain auxiliaries may be added. The most common is rosin or rosin derivatives. They are able to coat the particles as they are formed and prevent the growth of particles. Later, during the dispersion process it facilitates improved wetting of the particles, assisting their incorporation into the binder. Other auxiliaries are sometimes used which resemble the pigment molecule, but contain groups that have an affinity for the application media, again improving wetting and facilitating easier dispersion.

The first stage in the drying process consists of applying hydraulic pressure and squeezing out most of the water. This produces presscakes, but still contains between 45–70% water, so has limited application. Therefore, it is normal to dry the presscake. This drying process is almost a technology in its own right. It can be a long, slow process lasting as long as two days. The presscake is spread out as thinly as possible and dried on trays or on conveyer belts, using large steam-heated ovens. Pigments that are heat sensitive may be dried under partial vacuum.

Another method of drying involves the use of spray dryers, where the pigment paste is sprayed into a heated cone shaped chamber.

The dried pigment then has to be pulverized. Each pigment will have its own characteristics and too heavy a pulverization can lead to re-agglomeration.

Azo pigments can be manufactured as a batch process or on a continuous operation [4, p. 208].

Crude phthalocyanine, which is in the β form, can be converted to a pigment grade by a number of methods, depending on the crystal modification required. An important stage in conditioning is to dissolve some of the pigment in concentrated sulphuric acid. When added to cold water the α crystal form is produced. The presence of surface-active agents improves the quality.

The pigmentary grade can also be prepared by dry milling of the crude with a salt such as sodium chloride or sodium sulphate. The crude β grade slowly changes into the α form, but a complete conversion is not usually possible and commercial grades may contain around 10% of the β form. However, if a small amount of polar solvent is present, the β form is retained.

3.9 Toxicity and the environment

Pigment suppliers and paint chemists have a responsibility to protect their own health and the health of those who use their products, and the environment. However, ideas on how this can best be achieved with respect to people, animals, and plants are constantly changing. Suppliers have a responsibility to provide full information on their products, including their physiological properties and their effect on the environment. Details on how to handle pigments safely in the workplace and how to dispose of wastes should be given. This allows users to assess the hazards associated with such raw materials and formulate suitable handling procedures.

Compared with many other chemicals, most pigments are of low hazard, primarily because of their low solubility, which limits their bioavailability and hence their toxicity. However, as this is such a complex subject, the industry is vulnerable to scare stories, badly thought-out legislation, and misinformation. In an effort to overcome such problems the pigment manufacturers through their relevant industry associations, have made a great effort to be proactive in going beyond their legal

obligations and communicate the hazards associated with pigments and to explain in clear language some of the issues.

In 1993 the Color Pigments Manufacturers Association, Inc. (CPMA) published *Safe Handling of Color Pigments* [26]. In addition to providing details of most of the hazards associated with pigments, it explains many of the terms used in conveying safety information. It also details the legislation affecting pigments and details of the various agencies charged with the enforcement of such legislation in North America.

Outside North America, the industry recognized the contribution made by this publication and four organizations co-operated to produce a similar publication but with an emphasis on European legislation. In 1995 ETAD (representing organic pigment manufacturers), BCMA (representing the British pigment manufacturers), VdMI (representing inorganic pigment manufacturers and many users in Germany) and EPSOM (representing French pigment manufacturers) published *Safe Handling of Pigments* [2].

Both publications have been widely circulated throughout the pigment-using industry and provide an excellent starting point for anyone trying to achieve a better understanding of issues and concerns associated with the use of both organic and inorganic pigments and are therefore essential reading.

3.10 Choosing pigments

Before selecting a pigment for a specific paint the formulator needs to consider the type of paint being manufactured and its end use. The markets in which they are to be used may classify paints. The usual classifications are those used for buildings, either architectural or decorative, automotive finishes, either OEM (original equipment manufacturers) or VR (vehicle refinishes), and those used for industrial finishes. In addition there are powder coatings and coil coatings, both of which cover a range of demands.

3.10.1 Paint types

The binder in the paint system plays an important role in the selection of the pigment, in particular the solvent in which it is dissolved. Water is increasingly being used as a solvent and this makes relatively little demand on pigments, except for some toners. Long oil alkyd paints, as used in many decorative gloss paints, usually use white spirit as their solvent. Most pigments are insoluble, or almost insoluble in white spirit, so this rarely restricts the pigments one can select. General industrial finishes can be based on a whole range of solvents: many such as xylene, ketones, and esters are very powerful solvents and can dissolve pigments with poor or only moderate resistance to solvents. If such paints are dried by stoving, the elevated temperature makes even greater demands on the pigments used. One also has to consider if the coating is likely to be overcoated. It is safe to assume that most cars will at some time have to be repaired, so any pigment used in the original finish will have to be fast to overcoating.

In powder coatings many of the crosslinking agents can affect the pigment, so it is important to ensure the pigments are stable to these agents, at the temperatures likely to be employed during application.

The type of resin used and the solvent used for the resin therefore remain key factors in the choice of pigment.

3.10.2 Paint performance

Consideration has to be given to the end use of the paint, especially with respect to its durability requirements, any resistance to chemicals and the price that can be tolerated for improved performance. Clearly it would be as futile to use cheap, low-quality pigments in an automotive finish as it would to use a high-quality pigment in a paint that was to be used in a gardening implement! The difference between the price of a cheap organic pigment and one giving a high performance can be a factor of around 20. The speciality pigments developed for high performance are often very complex in nature and have limited application, hence their high price.

3.10.3 Opacity and transparency

In pale shades, the inorganic pigment used, usually titanium dioxide, normally provides the covering power. The influence of the coloured pigment is insignificant. However, deeper shades have a much lower proportion of titanium dioxide, hence one needs more opaque coloured pigments. Such shades are known as solid shades.

Certain special effects can only be achieved using transparent finishes. These include the metallic and pearlescent paints frequently used in automotive finishes. The aluminium or pearlescent pigments provide the covering power, but the coloured pigments used are required to have high transparency in order to allow the sparkle of the aluminium or pearlescent pigment to show through, giving clarity to the finish. This results in the paint appearing to have a different colour depending from which angle it is viewed, and hence the length of the light path through the coating. This is the so-called flip tone. Although dyes can be used, they rarely provide sufficient resistance properties. As the light passes through the film twice, this can make extra demands on light fastness, so only pigments with the highest standards of light fastness can be employed for such applications. Transparent pigments are also required in some clear lacquers such as flamboyant finishes that are used for bicycles, car coatings, or as wood stains.

The restrictions placed on certain inorganic pigments based on metals restricted by legislation have resulted in the search for safer inorganic pigments, or for more opaque organic pigments. Several organic pigments have been introduced that are characterized by high opacity, especially in the yellow, orange, and red parts of the spectrum. Conversely, iron oxide pigments can be prepared in a very fine particle form, resulting in their having high transparency. Transparent iron oxide pigments are frequently used in automotive finishes where they tend to lift the performance of brighter organic pigments as they are able to absorb UV radiation.

3.10.4 Colour and blending of pigments

Few colours, with the exception of black and white, can be matched with a single pigment. Instrumental methods for matching colours have simplified the

process, but a working knowledge of pigment technology is of great advantage before one chooses the products to be used, as few pigments find universal application.

Trying to keep the formulation simple and thereby using as few pigments as possible is a good principle. In a pigment blend, solvent resistance depends on the worst pigment present. Likewise, the pigment with the worst light fastness has a disproportionate effect on the light fastness of the total system, e.g. a pale orange made from CI Pigment Yellow 74 and CI Pigment Red 3 will rapidly fade towards the yellow side because of the inadequate fastness of the red.

Purity of shade is also a factor one must consider. It is normal to use dull pigment, such as iron oxide, and tint to the required shade with a brighter organic pigment, thus utilizing the economy and the fastness of the iron oxide to the maximum. When bright colours are mixed together, the resulting shade becomes duller the further they are from each other in the spectrum, hence blue and red give dull purple (or maroon) shades, whereas red and violet gives a much brighter purple shade.

Another consideration when blending pigments is the avoidance of using mixtures of pigments with wide differences in particle size, as this can give rise to flotation and flooding. This effect can often be seen in grey paints based on carbon black (as small as $0.01\text{ }\mu\text{m}$) and titanium dioxide ($0.25\text{ }\mu\text{m}$).

3.10.5 Quantity of pigments in a paint

The amount of pigment used in a paint is determined by:

- its intensity and tinctorial strength;
- the required opacity;
- the gloss required;
- the resistance and durability specified.

The paint technologist works on one of the two main concepts, either pigment volume concentration (PVC) or pigment to binder ratio (P:B). The PVC is of fundamental concern when formulating paints that are required to have optimum performance with respect to durability. It is known that there is a critical point that represents the densest packing of the pigment particles commensurate with the degree of dispersion of the system [27]. It is a complex calculation but essential for paints that have to meet the highest performance standards with respect to durability.

The P:B ratio, by weight or occasionally by volume, is a much simpler calculation, often used to assist in formulating a good millbase and for balancing a formulation for gloss and opacity.

For systems requiring high gloss, a low PVC is required, whereas primers and undercoats can have a much higher PVC — up to 90%.

3.11 Physical forms of pigment

Most pigments are supplied as free-flowing powders, although some are supplied as low-dusting granules. However, there are several other forms available depending on the requirements of the paint manufacturer.

3.11.1 Pigment preparations

As pigments have become more complex in nature and the systems into which they are incorporated have become more numerous and complex, traditional dispersion techniques have not always proved satisfactory. The best example is in water-based emulsion paints. Although one can disperse titanium dioxide and extenders into emulsion systems, it is much more difficult to disperse organic or even coloured inorganic pigments into the resin without affecting the properties of the resin itself. Therefore, such pigments are normally dispersed into a non-ionic and/or anionic surfactant system and added to the paint as a paste. The pigment manufacturer, the paint manufacturer, or a third party specializing in such products can produce these pastes.

Such aqueous preparations are required to have a high degree of compatibility and should be resistant to drying out. Most organic pastes will contain around 40–55% pigment content, iron oxide pastes can have a much higher pigment content, but carbon black pastes are usually much lower.

Multi-purpose pastes are a natural progression from such products. As well as having good compatibility with emulsion paints, they can also be used for the coloration of air-drying alkyd paints. This is achieved by using surfactants that not only act as dispersing agents and aid compatibility in emulsion paint, but also act as emulsifying agents in solvent-based systems. Again they can be supplied by certain pigment producers, made by the paint manufacturer or supplied from a third party. These colorant pastes are the basis of the tinting systems frequently seen in large paint retailers, providing a much greater selection of shades than would be available in a ready mixed range.

Certain paint systems require very high degrees of dispersion. This is frequently necessary in automotive metallic shades and specialist companies are able to provide such a service. Also in the general industrial area, there is an increasing demand for pigments that offer a wide range of compatibility, allowing the paint manufacturer to concentrate on producing high volumes of base paints and tinting to shade with stainers.

3.11.2 Presscake

Most pigments are synthesized in an aqueous system. The pigment then has to be dried, a costly operation. However, many applications are water based. Earlier presscakes contained around 70% water and felt like damp powders, but it is now possible to extract a much higher proportion of water using hydraulic and vacuum techniques, making presscakes with as little as 40% water available. Such products are primarily of interest to aqueous preparation manufacturers.

3.11.3 Flush pastes

Organic pigments in the form of flush pastes are now widely used for the production of offset inks. If the pigment presscake is mixed with a binder, such as linseed oil, and thoroughly mixed in the presence of selected surfactants, the pigment eventually transfers from the aqueous phase to the oil phase. Such pigment pastes have undergone little agglomeration and aggregation, so they are relatively easy to disperse. As the end user has little control on the binder, flush pastes have very limited use in the paint industry.

3.11.4 Masterbatch

Most plastics, especially polyolefins and engineering polymers, are coloured with masterbatch. These are either single pigments or blends to a certain standard shade, which are highly dispersed in a suitable medium, allowing consistent and easy coloration of polymers. This approach is finding favour with manufacturers of powder coatings and can also include the incorporation of other ingredients, such as stabilisers. However, to date most manufacturers continue to start from powder pigments.

3.12 Notes on families of pigments

In this section some of the more important pigment types are briefly described and compared. The information cannot be complete, and should only be used in conjunction with manufacturers' data and tests in the system being used. The pigments are grouped in colours, but there can be some overlap, so for instance, while most orange pigments are detailed under orange, some may appear in the red or yellow sections, if their chemistry better fits these colour areas.

3.12.1 White pigments

All pigments in this sector are inorganic and it is totally dominated by titanium dioxide, or more correctly titanium (IV) oxide. It was first manufactured in 1916, developed through the 1930s, but only became the dominant white pigment after the Second World War. It has largely displaced other white pigments. Whereas coloured pigments are compared by their tinctorial strength, in the case of white pigments the reducing power is used as the comparison. This is the amount of white pigment needed to produce an equal depth of shade when used with a standard amount of coloured pigment.

- Titanium dioxide
- White lead
- Zinc oxide
- Zinc sulphide
- Lithopone
- Antimony oxide

3.12.1.1 Titanium dioxide

Colour Index — CI Pigment White 6.

Formula — TiO_2 .

Titanium dioxide exists in three crystal forms: *brookite* is not used as a pigment, *anatase* is only used occasionally and is softer in texture and has a slightly better white colour than the most commonly used crystal form *rutile*. However, rutile has a higher refractive index (around 2.76 compared with around 2.55 for anatase) and is therefore more opaque and it has much less tendency to chalk (see section 3.6.1).

Modern grades have much better chalk resistance imparted by treating the photoreactive sites on the surface of the crystals with inorganic oxides, such as those of aluminium, silicon and zinc.

Two different processes are used to manufacture the rutile grade. The sulphate method is the older and starts from the ore ilmenite. Ferrous sulphate and dilute sulphuric acid are by-products of the process, and it is their disposal that has caused environmental problems. Pigments produced by this method used to be slightly stained by the iron salt, giving it a slightly yellow colour, but this is no longer necessarily the case.

The more modern chloride process commences with the ore of titanium dioxide called rutile. The ore is mixed with coke ground to a powder. It is then reacted with chlorine at temperatures around 900°C, to form titanium tetrachloride, along with oxides of carbon. Titanium tetrachloride is a liquid and can be condensed, separating off impurities. The purified titanium tetrachloride is vaporized, superheated, and reacted with oxygen at around 1500°C. The chlorine that is given off is recycled.

Titanium dioxide possesses many of the ideal properties demanded of a white pigment. It has a good white colour and very high resistance to organic solvents, most chemicals, and heat. However, it is its high refractive index which makes it such an attractive pigment, allowing the production of highly opaque coatings. It has good durability and is unaffected by industrial atmospheres. Its photoreactivity does reduce the light fastness of some coloured pigments, including almost all organics.

Early grades suffered from poor dispersibility, but again coating the pigment particles can produce much-improved commercial products. The balance between dispersibility and durability generally requires products that are specific to a range of applications, such as water-based paints or solvent-based stoving finishes. Being inert, it has favourable physiological properties and can be used for food packaging, toys, and other sensitive applications, providing it meets purity criteria [28].

In spite of its excellent properties, titanium dioxide is reasonably priced. Nevertheless attempts are made to replace or partially replace it with cheaper pigments or semi-opaque extenders.

3.12.1.2 *White lead*

Colour Index — CI Pigment White 1.

Formula — $2\text{PbCO}_3\text{Pb(OH)}_2$.

This pigment reacts with acidic binders giving tough elastic films, which have good durability, especially on woodwork. However, the pigment also reacts with the sulphurous gases in industrial atmospheres and goes black. Concerns regarding the toxicity of lead compounds severely limit its use.

3.12.1.3 *Zinc oxide*

Colour Index — CI Pigment White 4.

Formula — ZnO .

Zinc oxide can also react with binders by producing zinc soaps in oleoresinous paints, which confer hardness and resistance to abrasion and moisture, but can cause severe thickening in the can. It gives some mildew resistance in paints and reduces the breakdown in binders, which results in chalking, so can be a minor component of titanium dioxide. It was widely used before the introduction of titanium dioxide, but its use has now declined.

3.12.1.4 Zinc sulphide

Colour Index — CI Pigment White 7.

Formula — ZnS .

This pigment produces a good, strong white, good opacity and a high degree of chemical inertness. However, it chalks badly.

3.12.1.5 Lithopone

Colour Index — CI Pigment White 5.

Formula — either ZnS 30% / BaSO_4 70% or ZnS 60% / BaSO_4 40%.

These pigments were available before zinc sulphide. Their properties follow those of zinc sulphide, but are correspondingly weaker owing to the barium sulphate content. They also have poor resistance to chalking. They are relatively cheap and sometimes partially replace titanium dioxide.

3.12.1.6 Antimony oxide

Colour Index — CI Pigment White 11.

Formula — Sb_2O_3 .

Originally used to reduce the chalking of anatase titanium dioxide, this pigment is inert and moderately opaque. Its main use today is in fire-retardant paints.

3.12.2 Black pigments

Carbon black is the most common black pigment, although there are a couple of organic blacks, one based on anthraquinone, and also a black iron oxide. Within the term carbon black there is a wide variety of types available:

- Carbon black
- Graphite
- Black iron oxide
- Micaceous iron oxide

There are also a couple of organic black pigments:

- Aniline black — CI Pigment Black 1
- Anthraquinone black — CI Pigment Black 20

3.12.2.1 Carbon black

Colour Index — CI Pigment Black 6, 7, 8.

Formula — C (Carbon).

Carbon black is one of the oldest of pigments, being used by early man in cave paintings 27000 years ago, by the Egyptians as far back as 2500 BC in inks, then through the Middle Ages when the printing process was first developed. They are manufactured by thermal oxidative dissociation of hydrocarbon oils or gas. Although carbon blacks are inorganic, they have many of the properties of organic pigments. They consist of elemental carbon, but there is a wide variety of products available, dependent on the starting materials and method of manufacture. The grade of carbon black selected must be matched to its particular field of application, as commercial grades are manufactured to carefully defined requirements. The paint industry is only a modest user of these pigments. By far the biggest user is the

rubber industry, where carbon black not only imparts colour but also increases the strength and is therefore an essential component in tyres. The printing inks industry also uses significant quantities.

These pigments have excellent light fastness and good resistance to solvents, although in some of the cheaper pigment grades, solvents can extract some coloured impurities. Chemical stability and heat stability are excellent. The particle size determines the intensity of blackness, known as jetness, smaller particles giving higher values. There is an internationally recognized scale used to classify carbon blacks, signifying the manufacturing process and the jetness.

The first two letters designate the colour strength of the pigment; high colour (HC), medium colour (MC), regular colour (RC), and low colour (LC). The final letter describes the manufacturing process; furnace (F) and channel/gas process (C):

				Range of average particle sizes
HCC	High colour channel	HCF	High colour furnace	0.010–0.015 μm
MCC	Medium colour channel	MCF	Medium colour furnace	0.016–0.024 μm
RCC	Regular colour channel	RCF	Regular colour furnace	0.025–0.035 μm
		LCF	Low colour furnace	>0.036 μm

The manufacturing process used to produce channel blacks consists of burning petroleum gases from several small jets in an atmosphere deficient in oxygen. The flame plays on rollers and the deposit is scraped off. This process is now almost defunct because it had disastrous consequences on the environment, producing severe air pollution and also because it is less economic.

Furnace blacks are produced by the thermal oxidative process, which involves burning hydrocarbon oils with a high aromatic content, using a single flame, in a limited supply of air. The carbon is collected by electrostatic precipitation. Particles produced by this process lie between 0.01 and 0.08 μm.

The finer particle blacks are used for high-quality finishes such as in automotive paints on account of their higher jetness. Medium size blacks are used for intermediate quality paints, whereas the coarser pigments are used for decorative paints. For tinting purposes coarser grades are usually used as their lower strength means they are easier to control. As the carbon black is in the form of a light dusty powder, it is often converted to an easy to disperse pellet form by the dry pelleting process.

Carbon black pigments can cause problems in paint as over a period of time they absorb active ingredients in the formulation, such as the metal soaps used as driers in air-drying alkyds. It is normal to double the drier content to compensate. Another problem is that being such small particles they have a tendency to flocculate after dispersion. This can be minimized by taking great care when diluting paints. Only small stepwise additions should be made with thorough homogenization between additions.

Carbon black, having very small particles with a corresponding large surface area, can prove difficult to disperse. The dispersibility can be improved by slightly oxidizing the surface of the pigment (this can be shown in the designation by the suffix 'o', e.g. HCC[o]) or by the addition of small quantities of organic groups such as carboxylic acids. Such groups reduce the pH of the aqueous extract and aid the wetting of the particles. Another problem associated with paints having a high proportion of carbon black is structure. The particles of carbon appear to form clusters,

often compared to a cluster of grapes, held together by forces ranging from weak physical attraction to chemical bonds. This structure affects the dispersibility, the jetness, gloss, and, most of all, the viscosity of the paint.

Although the price of carbon black varies considerably, generally increasing as the particle size decreases, it is a relatively cheap pigment largely because of the very large quantities manufactured for the rubber industry. Speciality grades made for specific applications are more expensive because there is less economy of scale.

3.12.2.2 *Graphite*

Colour Index — CI Pigment Black 10.

Formula — C, elemental carbon crystallized in a hexagonal system.

Graphite is the traditional 'lead' in pencils. It is a soft pigment consisting of inert plate-like particles. These lamellar plates form layers in a paint film, which prevent the penetration of water and are therefore used to reinforce other pigments in anti-corrosive paints. As it has low tinctorial strength and its colour is of low intensity, it is not used for its colour, but it does confer high spreading rates owing to the slippery nature of the particles.

Graphite can be obtained from natural sources, in varying levels of purity from 40 to 70% in combination with silica. It can also be manufactured by the Acheson process, which consists of heating anthracite in electric furnaces at high temperatures.

3.12.2.3 *Black iron oxides*

Colour Index — CI Pigment Black 11.

Formula — ferrous-ferrous oxide FeO , Fe_2O_3 .

This pigment occurs naturally as magnetite and can be used in its natural form. However, like most iron oxide pigments used in paint, it is now usually manufactured synthetically. It is a cheap, inert pigment with excellent solvent and chemical resistance, and excellent durability. It has limited heat stability and low tinctorial strength.

Its main use is for applications where the tendency of carbon black to float, especially in grey tones in combination with titanium dioxide, cannot be tolerated. Its lower tinting strength can also be an advantage when used as a tinter, as it allows more control.

3.12.2.4 *Black micaceous iron oxides*

Colour Index — no listings.

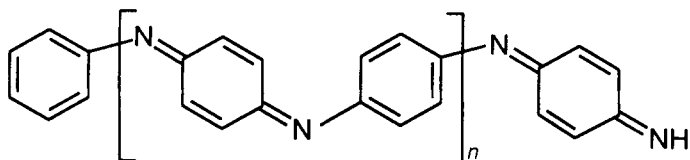
Formula — lamellar shaped particles of Fe_2O_3 .

Its main use is in heavy-duty coatings to protect structural steelwork, where its plate-like structure impedes the passage of oxygen and moisture. It is inert and its ability to absorb to UV radiation also protects the polymers used as binders. It has a greyish appearance and a shiny surface, not unlike mica, hence its name. Care must be taken not to over-disperse because the platelets can be broken and rendered ineffective.

3.12.2.5 *Aniline black*

Colour Index — CI Pigment Black 1 (however, the structure given is not considered adequate).

Formula — azine structure:



Aniline black is probably the oldest synthetic organic pigment. It was discovered around 1860 and is not dissimilar to a product with the same name discovered by Perkin, who is regarded as the father of organic dyes and pigments. It is used in some speciality coatings where very deep blacks are required, which it achieves because of its low scattering power and very strong absorption of light. It has a very high binder demand so produces matt effects in paint, often described as velvety in appearance. Its fastness properties are quite good, but its chromium (VI) content limits its application where physiological properties have to be considered.

3.12.2.6 Anthraquinone black

Colour Index — CI Pigment Black 20.

This pigment is used only in camouflage paints, because its infrared spectra satisfies various standards. It has moderately good light fastness and only moderate solvent resistance.

3.12.3 Brown pigments

This area is dominated by iron oxide, but a few organic pigments are used for speciality applications.

- Iron oxides — CI Pigment Brown 6 (synthetic), 7 (natural)
- Metal complex — CI Pigment Brown 33
- Benzimidazolone — CI Pigment Brown 25
- Azo condensation — CI Pigment Brown 23, 41, 42

The azo browns will be considered in the red section (section 3.12.6).

3.12.3.1 Iron oxide brown

Colour Index — CI Pigment Brown 6, 7.

Formula — Fe_2O_3 , ferric oxide.

When this pigment is derived from its natural form it is known as burnt sienna or burnt umber. Pigments are made from naturally occurring ores that are then heated. The various shades obtained are dependent on the impurities, especially the manganese oxide content. The names are familiar more by their use for artists' colours than from their use in commercial paints. They have low tinting strength and are not opaque.

The synthetic grades give a rich brown colour with excellent fastness properties, but do command a premium over yellow and red oxides. They are not used to any extent in paint formulations, as similar shades are more economically obtained using mixtures of cheaper pigments.

3.12.3.2 *Metal complex brown*

Colour Index — CI Pigment Brown 33.

Formula — $(\text{Zn, Fe}) (\text{FeCr})_2\text{O}_4$ in a spinel structure.

This pigment is used mainly in ceramics, but can be used in coil coatings, where its high heat stability and excellent fastness properties make it a useful pigment.

3.12.4 **Yellow pigments**

There are a large number of pigments in this part of the spectrum, both organic and inorganic. The choice depends on the end application with respect to brightness of shade, opacity, fastness requirements, physiological properties, and economic considerations. As well as being used in yellow paints, yellow pigments are also used in oranges, greens and browns, so it is a very important sector for the paint technologist.

Inorganic:

- Lead chromate
- Cadmium yellow
- Yellow oxides
- Complex inorganic colour pigments (mixed phase metal oxides)
- Bismuth vanadate

Organic:

- Arylamide
- Diarylide
- Benzimidazolone
- Disazo condensation
- Organic metal complexes
- Isoindolinone
- Isoindoline
- Quinophthalone
- Anthrapyrimidine
- Flavanthrone

3.12.4.1 *Lead chromate*

Colour Index — CI Pigment Yellow 34, Orange 21.

Formula — $\text{PbCrO}_4/\text{PbSO}_4$; the orange is $\text{PbCrO}_4 \cdot x\text{Pb}(\text{OH})_2$.

These pigments can be pure lead chromate or mixed phase lead chromate and lead sulphate. They can range in shade from a greenish yellow through to orange. The most important pigments are:

- Primrose chrome — a pale, greenish yellow (containing between 45% and 55% lead sulphate), where the pigment has a metastable orthorhombic structure crystal structure, which needs to be stabilized by the addition of additives.
- Lemon chromes — still a greenish yellow, but somewhat redder than primrose, depending on the sulphate content (it contains between 20% and 40% lead sulphate, the more sulphate, the greener the shade). It has a monoclinic crystal structure.

- Middle chromes — reddish yellow, mainly pure lead chromate precipitated in the monoclinic structure.
- Orange chrome — chemically this pigment is basic lead chromate and contains no sulphate. It has a tetragonal crystal structure. Varying the proportion of 'x' in the formulation can alter the shade, but the crystal structure also plays a role.

Lead chromes are noted for their excellent opacity, low oil absorption, very bright shades, and high chroma (i.e. they give deep or saturated shades), making them ideal for full shade yellow paints. They also possess excellent solvent resistance and moderately good heat stability, which can be further improved by chemical stabilization. They are sensitive to alkalis and acids, including industrial atmospheres, which cause them to fade. Their light fastness is usually satisfactory in full shade, but they darken on exposure to light. All these deficiencies can be much improved by surface-treating commercial grades with such material as silica, antimony, alumina, or various metals.

The one drawback that severely limits the wider use of these pigments is that they contain both lead and chromium (VI). This effectively limits their application to certain industrial finishes [2, Section 3.7]. In Europe, paints containing these pigments are required to carry warning labels. When being used for paint manufacture, careful attention must be paid to the handling instructions contained in the safety data sheets. Disposal of waste can also be problematic and local regulations carefully followed.

They are relatively cheap to use and replacing them especially in full shade formulations cannot be achieved without a considerable increase in cost.

3.12.4.2 *Cadmium yellow*

Colour Index — CI Pigment Yellow 37, 35 (lithopone type).

Formula — CdS, cadmium sulphide, containing some zinc sulphide. The lithopone type contains barium sulphate.

The relatively high price of cadmium pigments has always limited their use in paints, but they do possess excellent heat stability, solvent fastness, and alkali stability. They have good light fastness in full shades, but fade in reductions and discolour in industrial atmospheres. They have excellent opacity and offer bright colours with high chroma.

In Europe, their use in almost all coatings is prohibited, owing to the environmental problems associated with cadmium.

3.12.4.3 *Yellow iron oxide*

Colour Index — CI Pigment Yellow 42 (synthetic), 43 (natural).

Formula — $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, hydrated ferric oxide (or more correctly $\text{FeO}(\text{OH})$).

Yellow iron oxide is by far the most important coloured inorganic pigment used in the paint industry. It occurs naturally as limonite, but is better known as raw sienna or yellow ochre. It ranges in shade from a bright yellow to very dull yellow depending on the purity. Natural grades have been used as pigments since humans lived in caves and are still widely used for colouring concrete, but in the paint industry the synthetic grades predominate.

There are various routes for its synthesis. It has a needle-like shape (acicular) and the final colour is dependent on the dimensions of the crystal. The longer the

needle, the greener and purer the colour. The greener grades can be overdispersed, which results in the crystals breaking and changing colour. The crystals can exist in three forms, α , β , and γ , but it is the α form that predominates.

These pigments are almost perfect for the paint manufacturer, except for one limitation. Unfortunately, this limitation is their colour. They are very much duller than either lead chromes or organic alternatives. Nevertheless, it is normal to utilize their excellent application properties with their relatively low price as far as possible and then tinting to shade using brighter alternatives. They are the basis of most 'magnolia' decorative shades, through to high-quality beige industrial colours.

They have excellent resistance to solvents and chemicals. They have moderate tinting strength, but this can be an advantage, as it requires relatively little organic pigment to brighten them. Their light fastness and durability is excellent; in addition they even improve the light fastness of other pigments with which they may be combined and the polymers in which they may be incorporated, as they absorb damaging UV radiation. They have a high refractive index so normally have good covering power, but can be manufactured in a transparent form. They are among the easiest of pigments to disperse. The only technical property, which limits their application, is their heat stability. Above 105 °C they start to lose water of crystallization, giving a shade shift towards red, and this accelerates as the temperature and/or time of exposure are increased.

Transparency is achieved by preparing the pigment in as fine a particle size as possible by:

- controlling precipitation under special conditions; and
- attrition in high-energy mills.

Transparent grades are much more difficult to disperse, so are often sent to dispersion houses, where special techniques are employed to maximize transparency. They are much more expensive than conventional grades, but are widely used for automotive metallic shades and transparent wood finishes.

3.12.4.4 *Complex inorganic colour pigments (formerly known as mixed phase metal oxides)*

Colour Index — CI Pigment Yellow 53, 119, 164, Brown 24.

Formula — three of these pigments have a rutile titanium dioxide structure, with another metal oxide trapped in the crystal lattice.

These pigments were formerly known as 'mixed phase metal oxide', but this name implies that these pigments are mixtures of metal oxides. This is not the case; they are in a homogeneous chemical phase, in which a host lattice traps a 'foreign' cation. CI Pigment Yellow 53 is derived from the rutile titanium dioxide crystal lattice, in which there is a partial replacement of the Ti^{4+} ions with Ni^{2+} ions, at the same time incorporating antimony (V) oxide such that the Ni/Sb ratio is 1:2. A typical composition of this pigment might be $(\text{Ti}_{0.85} \text{Sb}_{0.105} \text{Ni}_{0.05}) \text{O}_8$.

These pigments were formerly developed for the coloration of ceramics and are often referred to, incorrectly, as titanates. They have excellent solvent fastness and heat stability. Their light fastness is good to excellent and they have good chemical stability (although zinc ferrite brown is less stable). The earlier grades were difficult to disperse, but more recent commercial products are much improved. Their opacity is good but much lower than titanium dioxide. They have quite low tinctorial

strength and are relatively expensive. These pigments are being used for high-quality applications such as automotive and coil coatings, often in combination with organic pigments, to provide medium to full shade alternatives to chrome pigments. They can also be used alone for pale shades. Although they may contain heavy metals such as nickel, chrome, and antimony, which may pose threats to the environment, these pigments are so inert they can be regarded as physiologically and environmentally harmless.

3.12.4.5 *Bismuth vanadate*

Colour Index — CI Pigment Yellow 184.

Formula — between BiVO_4 and mixed crystals of BiVO_4 and Bi_2MoO_6 .

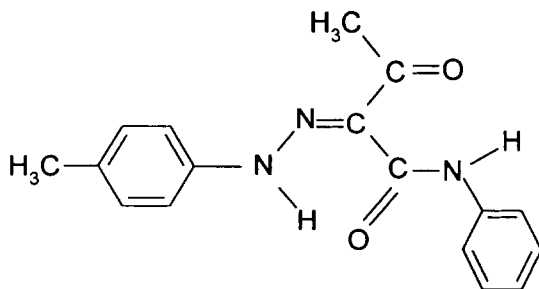
This pigment, which has only been on the market for a relatively short time, could arguably be included in the above category, but its manufacture and application characteristics are somewhat different. It is a bright, intense green shade yellow pigment. It possesses high opacity, high light fastness, and excellent solvent and heat resistance. It can be used for high-quality applications such as automotive coatings, powder coating, and coil coatings. In combination with organic pigments it produces very bright shades with high chroma and high covering power. Relatively small proportions of organic pigment seem to have a dramatic effect on the resulting hue.

Early grades suffered from a serious defect in that they were photochromic, that is they changed shade in the presence of light, gradually returning to their original shade when the light source was removed. However, this problem has now been overcome by introducing inorganic stabilizers. They can be used for most high-quality applications, including automotive finishes, coil coatings, and powder coatings. They are relatively expensive, but economic in use. Toxicity studies indicate that the pigment can only be harmful at high concentrations, so low dusting grades minimize this risk. Current information suggests that they pose low risk to the environment.

3.12.4.6 *Arylamide yellow (Hansa® yellows)*

Colour Index — CI pigment Yellow 1, 3, 65, 73, 74, 75, 97, 111 (there are several other pigments in this group, but these are the more important grades).

Formula — as represented by CI Pigment Yellow 1, 'Yellow G'.



Arylamide pigments were discovered at the beginning of the twentieth century. Although there are many pigments in the group, they are characterized by moderate to very good light fastness, moderate tinctorial strength, poor to moderate solvent resistance and poor heat stability. Consequently, they are mainly used in

both water-based and white spirit-based decorative paints. Their nomenclature usually indicates their hue, 10G being very green, 5G being on the green side, G being virtually mid shade, whereas R and 3R (no longer commercially significant) are on the red side.

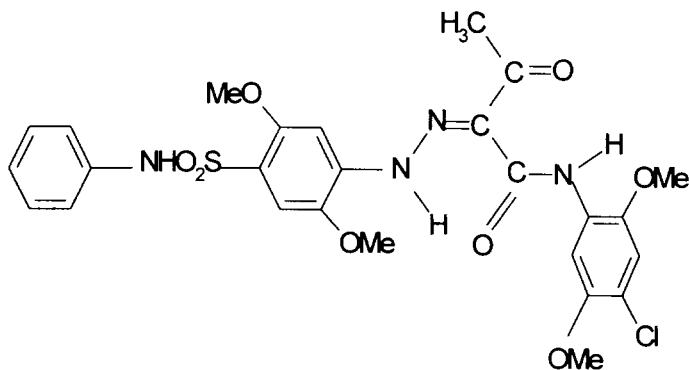
CI Pigment Yellow 3 (Yellow 10G) is one of the greenest in the series. The presence of two chlorine groups in the molecule gives it good light fastness, but it has low tinctorial strength. It is frequently offered in an easy to disperse form, which also possesses significantly higher colour strength than conventional grades.

CI Pigment Yellow 1 (Yellow G) is a mid shade yellow with moderate light fastness and moderate colour strength. Again it is frequently offered as an easily dispersible grade, with additional colour strength.

CI Pigment Yellow 73 (Yellow 4GX) is a mid yellow shade with similar colour and strength to Yellow G. Its main advantage is that it has significantly better resistance to recrystallization, an important consideration when dispersing in modern bead mills that can generate heat during the dispersion process, causing the pigment partially to dissolve.

CI Pigment Yellow 74 (Yellow 5GX) has grown in importance in recent years at the expense of Yellow G and 10G. It is available in various qualities. The conventional grade is approximately half way between G and 10G, but with much higher tinctorial strength. Its light fastness is close to Yellow G. As it is only slightly more expensive than Yellow G it is much more economic to use. Alternatively, it can be manufactured with a much larger particle size, resulting in a correspondingly higher opacity, making it ideal for full and near full shades. Although the colour strength is much reduced, it has much higher light fastness, and can therefore be used for pale shades.

CI Pigment Yellow 97 is not typical of these pigments:

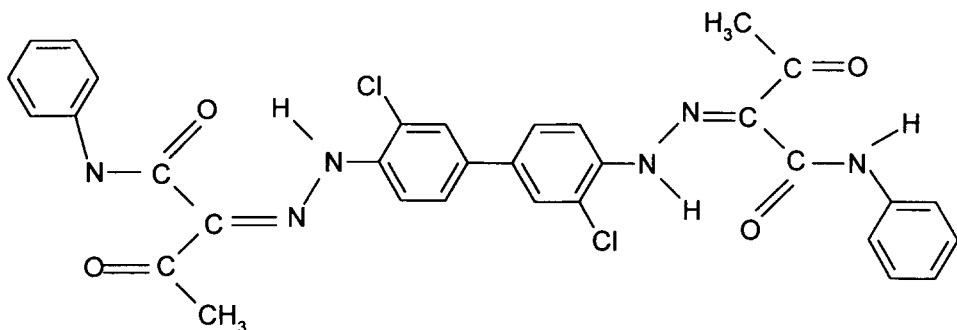


As one would expect from the extra benzene ring attached to the remaining molecule by a sulphonamide ($-\text{SO}_2\text{NH}-$), it possesses much better solvent fastness than other grades, and can be used in stoving enamels. Its light fastness is also very good and for a time it was used in automotive finishes. It commands a significantly higher price than the other arylamide yellows, which are relatively cheap.

3.12.4.7 Diarylide yellows (Disazo structure)

Colour Index — *CI Pigment Yellow 12, 13, 14, 17, 81, 83* (these are the most important members of the series but there are others).

Formula — as represented by *CI Pigment Yellow 12*:



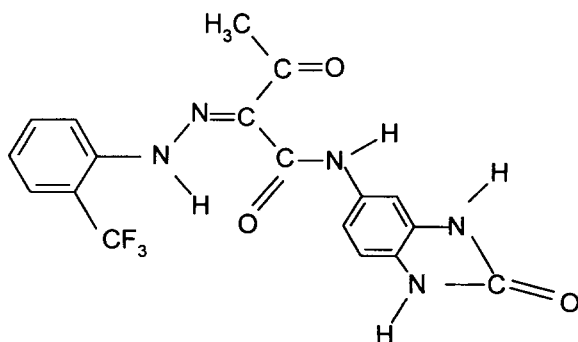
As these products are manufactured from 3, 3'-dichlorobenzidine, they used to be referred to as 'benzidine' yellows. This should be avoided as it confuses them with benzidine dyes, over which there are legitimate safety concerns. Providing they are not used above 200°C these pigments can be used. Diarylide pigments are the most important class of organic yellow pigments. However, this is largely because of their use in the printing ink industry, where they are the basis of the yellow process ink, used in three and four colour printing processes. They are characterized by high colour strength, good resistance to solvents and chemicals but poor light fastness. As they start to dissociate above 200°C they should not be used above this temperature. Their use in paints is limited by their poor light fastness, but some modern grades, especially CI Pigment Yellow 83, do find use in industrial finishes and powder coatings. In recent years a new CI Pigment Yellow 83 has been introduced in a larger particle size grade, which has high opacity and much improved light fastness. It is used as a replacement for middle chrome even for vehicle refinishing paints and commercial vehicle finishes.

Diarylide yellow pigments are relatively inexpensive and their high strength makes them very economic, but the more specialist grades are significantly more expensive.

3.12.4.8 Benzimidazolone yellows

Colour Index — CI Pigment Yellow 120, 151, 154, 175, 181, 194, Orange 36, 60, 62.

Formula — Represented by CI Pigment Yellow 154:



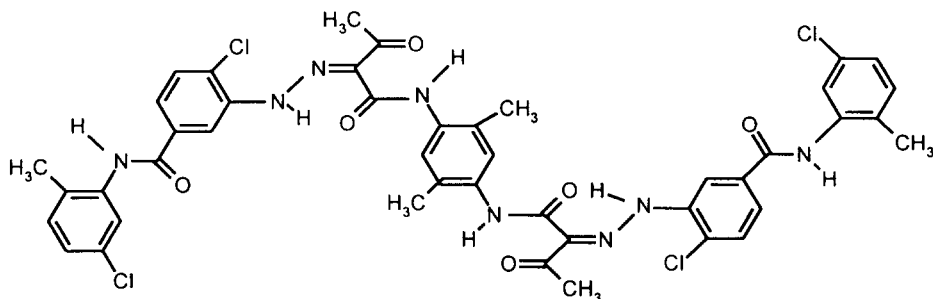
These pigments range in shade from a green shade yellow through to orange. They are mainly monoazo in structure, but when compared with other monoazo yellow pigments have much improved solvent resistance. This is due to the benzimidazolone group on the molecule, which is in effect a cyclical carbonamide group.

They are characterized by good to excellent light fastness, good solvent and chemical resistance, and good heat stability. Several grades are available in higher particle size forms, which improves light fastness even further and allows them to be used in demanding applications such as automotive finishes and powder coatings. Although significantly more expensive than other monoazo pigments, they are often more economic than other high-quality pigments in this part of the spectrum.

3.12.4.9 Disazo condensation pigments

Colour Index — CI Pigment Yellow 93, 94, 95, 128, 166.

Formula — Represented by CI Pigment Yellow 95:



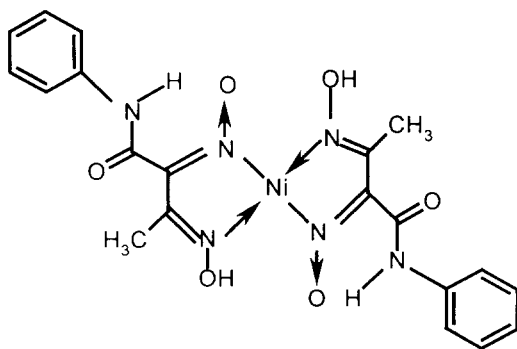
When discussing how it is possible to build solvent resistance to a molecule, two of the methods included building up the molecular size and introducing various insolubilizing groups such as the carbonamide group ($-\text{CONH}-$). The disazo condensation pigments utilize both approaches. This is achieved by putting together two acid derivatives of arylamide molecules, and condensing them by means of a diamine. This is not quite as easy as it sounds, but pigments produced in this way cover the whole of the spectrum from yellow, through orange and bluish red to brown.

As one would expect, such pigments have very good solvent resistance and excellent heat stability. They have reasonably good tinctorial strength and excellent chemical stability. They are relatively difficult to manufacture and therefore moderately expensive. Their main application is for the coloration of plastics, but individual products such as CI Pigment Yellow 128, are used in paints, including automotive original finishes.

3.12.4.10 Organic metal complexes

Colour Index — CI Pigment Yellow 129, 153, Orange 65, and 68. All azo methine complexes, and CI Pigment Yellow 150, Green 8 and 10. All azo complexes.

Formula — represented by CI Pigment Yellow 153:

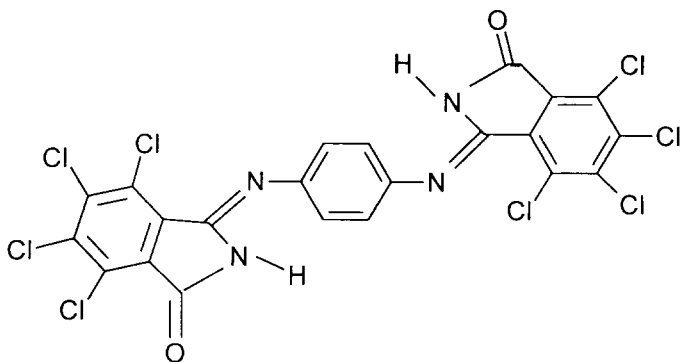


The introduction of a metal group into the molecule imparts solvent resistance into the pigment. This metal group can be the centre of the molecule as in azo methine complexes. The metals used can include nickel, cobalt (II), or copper. They are mostly rather dull in shade but transparent. However, one member of the group, CI Pigment Orange 68, is available in both transparent and highly opaque forms. Their main application areas vary, but several were used for automotive metallic finishes. In spite of the great expectations from this group of pigments, few have made a great impact on the paint industry, and few of the above-mentioned products remain commercially available.

3.12.4.11 Isoindolinone yellow pigments

Colour Index — CI Pigment Yellow 109, 110, 173, Orange 61.

Formula — represented by CI Pigment Yellow 110:

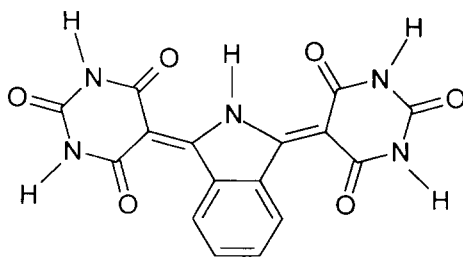


Isoindolinone pigments are chemically related to the *azo methine* types. Having already discussed how chlorine groups impart insolubility and promote light fastness in a molecule, it can readily be seen that these pigments are going to have excellent solvent resistance and good light fastness. They also have excellent chemical resistance and heat stability, making them ideal for plastics and high-quality paint systems, including automotive OEM, but also for pale decorative paints and tinting systems. They have only moderate tinctorial strength.

CI Pigment Yellow 173 still has an isoindolinone structure, but only has chlorine groups on the middle benzene ring, and therefore is lower in fastness properties. Nevertheless, it is still used in automotive metallic finishes, often in combination with transparent iron oxides. It is duller in shade than the other two yellows. CI Pigment Orange 61 is also less fast than the yellows. They are moderately expensive.

3.12.4.12 Isoindoline yellows

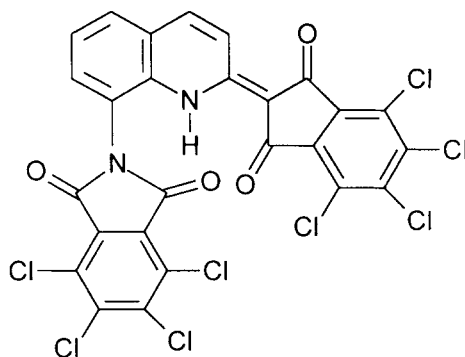
Colour Index — CI Pigment Yellow 139, 185, Orange 69.



Isindoline pigments are chemically related to the *methine* types. They have good general fastness properties especially for higher-quality industrial finishes. The yellows are not stable to alkalis. In general they are a little cheaper than the isindolinone pigments and have higher tinctorial strength.

3.12.4.13 Quinophthalone

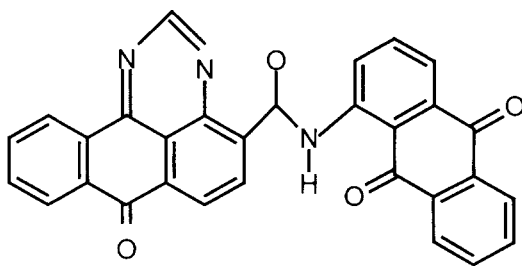
Colour Index — CI Pigment Yellow 138.



This pigment can be prepared in a highly opaque form that has a reddish yellow shade, possessing excellent light fastness and good resistance to solvents and heat. It is used as a chrome replacement in high-quality finishes. In its more transparent form it is much greener and has higher tinctorial strength, but with lower fastness properties.

3.12.4.14 Anthrapyrimidine

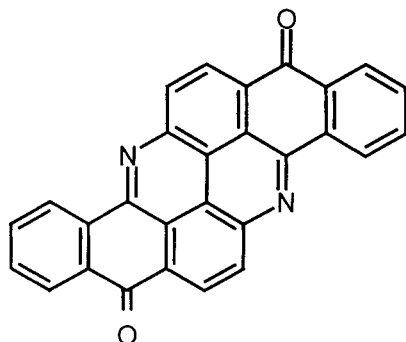
Colour Index — CI Pigment Yellow 108.



Anthrapyrimidine yellow was originally introduced as a vat dye (CI Vat Yellow 20), but as knowledge became available on how to treat the surface of these dyes in order to improve dispersibility, a process known as 'conditioning', a commercial grade of pigment was developed. For a period of time it was considered to be of the highest quality, but it has only moderately good resistance to solvents and its durability is not of the highest order, tending to darken when exposed to light. It is quite a dull colour and, although transparent, its light fastness is not good enough for today's automotive paints. Its complex nature makes it expensive.

3.12.4.15 *Flavanthrone*

Colour Index — CI Pigment Yellow 24.



This pigment was also known as a vat dye, but needs to be in a pure state and conditioned in order to obtain a commercial pigment. It is reddish yellow, stronger than anthrapyrimidine and with better heat stability. It is transparent and therefore is useful for metallic finishes where it shows good durability, although strong shades do darken on exposure to light.

3.12.5 **Orange pigments**

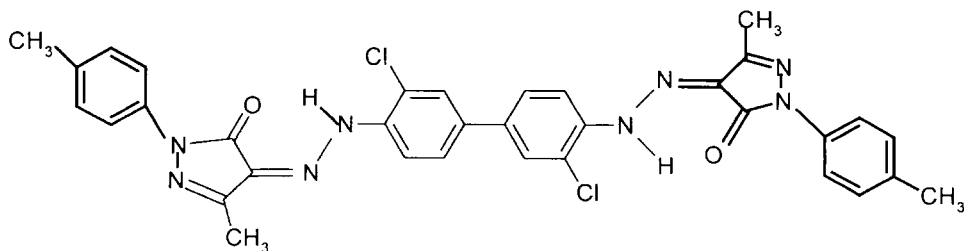
The borders between yellow/orange and orange/red are often difficult to define. Many orange pigments can be obtained following similar chemistry to the inorganic yellow chrome pigments, and to the arylamide, isoindolinone, and isoindoline yellow organic pigments. Others tend to possess chemistry more related to red pigments, such as molybdate and cadmium reds, β -naphthol and BON arylamide pigments. However, the following pigments stand in their own right as predominately orange pigments:

- Pyrazolone orange
- Perinone orange

3.12.5.1 *Pyrazolone Orange*

Colour Index — CI Pigment Orange 13, 34.

Formula — Represented by CI Pigment Orange 34:



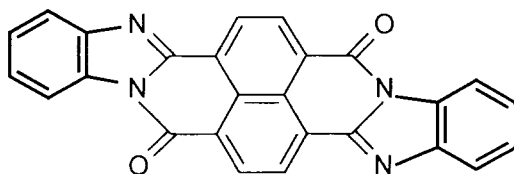
These pigments are closely related to the diarylide yellow pigments, and their properties are also similar. They are bright and have high tinctorial strength. Their solvent resistance and heat stability are moderate to good, but light fastness is poor. Therefore, their main use is for printing inks. The light fastness of CI Pigment Orange 34 is the better of the two and can be used in industrial finishes, especially when produced in its opaque form, making it a useful replacement for chrome pigments. They are reasonably cheap, so combined with their high strength, they are economic in use.

3.12.5.2 *Perinone orange*

Colour Index — CI Pigment Orange 43.

Perinone orange was developed as a vat dye (CI Vat Orange 7) and still finds a use for this application. It has a very bright shade and high tinctorial strength. It has excellent fastness to most solvents and has very high heat stability. Its light fastness is very good, but strong shades darken. It is a useful pigment for tinting systems on account of its brightness, strength and good properties. However, it is expensive to manufacture and its correspondingly high price limits its application.

Colour Index — CI Pigment Orange 43.



There is also a perinone red. The orange is the *trans* isomer whereas the red is the *cis* isomer. It is rather dull in shade and its fastness properties are somewhat lower. Although cheaper, it has limited application.

3.12.6 Red pigments

This is by far the largest colour group of pigments, and no one type predominates, perhaps reflecting that fact that all the chemical types in this part of the spectrum have major limitations. It is therefore essential that the paint technologist has a good knowledge of the products available, their strengths and limitations, as a well-informed selection will provide technical and commercial advantages. The most important types are as follows.

Inorganic:

- Lead molybdate
- Cadmium red
- Red iron oxide

Organic:

- β -naphthol
- BON arylamides

- Toners
- Benzimidazolone
- Disazo condensation
- Quinacridone
- Perylene
- Anthraquinone
- Dibromanthrone
- Pyranthrone
- Diketopyrrolo-pyrrole pigments (DPP)

3.12.6.1 *Molybdate red (or orange), scarlet chrome*

Colour Index — CI Pigment Red 104.

Formula — $\text{Pb}(\text{Cr}, \text{S}, \text{Mo}) \text{O}_4$, mixed-phase crystals of lead chromate, lead sulphate, lead molybdate in a tetragonal structure.

The shades vary from orange to intense scarlet. They are bright and have good opacity, excellent solvent resistance, and good durability, especially grades that have been stabilized. Heat stability is also good, but more demanding applications require stabilized grades. Alkali stability is only moderate. They disperse easily; indeed over-dispersion can damage their surface treatment and reduce their resistance properties. Molybdate red pigments are frequently used in combination with organic pigments to extend their colour range considerably, while maintaining excellent opacity. They are relatively cheap and would be the ideal pigment if it were not for their lead and hexavalent chromium content, which in Europe restricts their use to mainly industrial finishes.

It is necessary to comply with strict labelling regulations for both the pigment and paints made from these pigments.

3.12.6.2 *Cadmium red*

Colour Index — CI Pigment Red 108, Orange 20.

Formula — CdS/CdSe .

These pigments are bright and opaque and have excellent solvent resistance and heat stability. Their light fastness is good but they are not stable to acids, or industrial atmospheres. Cadmium pigments are relatively expensive and have only moderate tinctorial strength. Their use in most coatings is prohibited on physiological and environmental grounds.

3.12.6.3 *Red iron oxide*

Colour Index — CI Pigment Red 101 (synthetic), 102 (natural).

Formula — Fe_2O_3 Ferric oxide.

This pigment in the form of the mineral 'haematite' was used in the cave paintings found in Spain and France. It can be manufactured from the yellow 'raw sienna' by calcining and driving off the water of hydration. However, most red oxides used in paint are made synthetically by a number of manufacturing processes, each imparting its own specific characteristics on the resulting pigment. The shade is

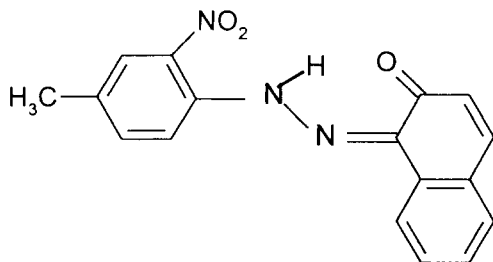
dependent on the particle size and shape, smaller particles giving a paler shade. The shape of the crystal can be influenced by seeding with appropriate crystals and by the degree of calcination.

Red iron oxides have excellent application properties. They have excellent heat stability, resistance to chemicals and solvents. Heat stability is excellent and they are normally opaque. They have quite low tinctorial strength, but in spite of this their low price makes them very economic in use. Providing they are purified, they appear to be physiologically harmless and have good environmental properties. It is possible to over-disperse them, which can make them darker in shade but as they are relatively easy to disperse, this should not be necessary. They do tend to settle in low-viscosity systems. Their only real limitation is their colour—they have a dull brownish red shade.

3.12.6.4 *β-Naphthol reds*

Colour Index — CI Pigment Red 3, 4, and Orange 5.

Formula — represented by CI Pigment Red 3:



β-Naphthol red pigments have a limited colour range from orange to mid red. For paint, two products predominate, toluidine red (CI Pigment Red 3) and dini-troaniline orange (CI Pigment Orange 5). Both pigments can be prepared in a range of shades depending on the particle size distribution of the commercial products, which in turn depends on the manufacturing conditions.

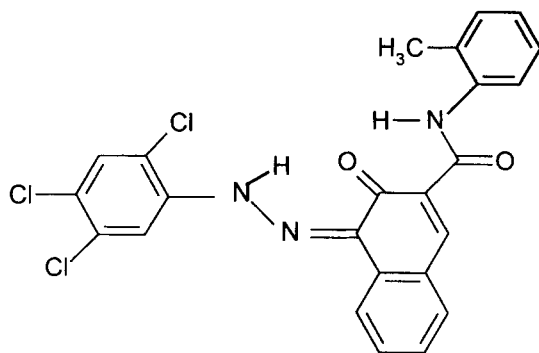
The nitro group plays an important part in the molecule, imparting both insolubility and light fastness. However, the improvement is relative, the molecule is a very simple one and consequently has limited solvent resistance and heat stability. Light fastness is reasonably good in full, or near full, shades, but falls off rapidly in paler shades. Chemical stability is generally good. These pigments are relatively cheap and therefore find application in both solvent-based and water-based decorative paints as well as cheap industrial paints, where good gloss retention is not essential.

For more demanding applications, they have been replaced with Naphthol AS® pigments.

3.12.6.5 *Naphthol AS® pigments (also known as BON arylamide pigments)*

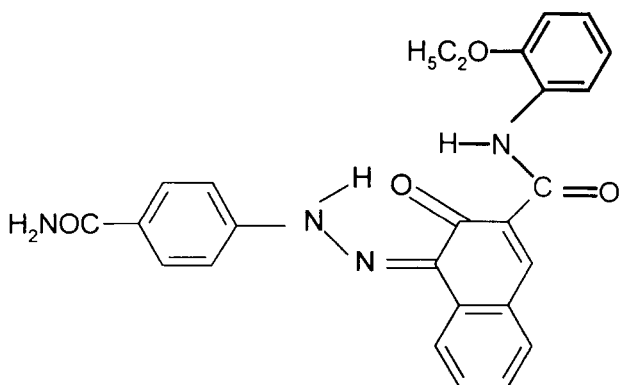
Colour Index — CI Pigment Red 2, 5, 12, 23, 112, 146, 170, Orange 38. These are the most important pigments used in paint; there are many other pigments in the series.

Formula — as represented by CI Pigment Red 112:



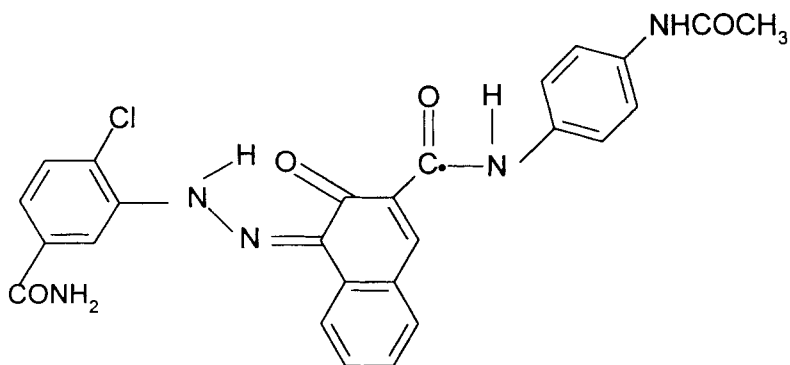
The addition of an extra benzene ring on this molecule has three effects on the pigment's properties. It increases the molecular weight, thus improving solvent resistance (the addition of a carbonamide group also improves insolubility). Finally, the extra benzene ring provides additional sites for further substitution that can alter the shade, improve solvent resistance and/or improve light fastness.

Consequently, Naphthol AS® pigments cover the spectrum from orange, through scarlet to bordeaux. Their properties can also vary considerably. They possess good chemical stability, but some of the pigments have only limited light fastness and solvent resistance, whereas others attain good general fastness properties. To some extent, properties can often be predicted from the structure. The pigment represented above, CI Pigment Red 112, has good light fastness and solvent resistance. It is used in decorative paints, including tinter systems, and cheaper industrial paints. It is available in a high-strength version or as a highly opaque grade. However, for industrial paints, including vehicle refinishing systems, CI Pigment Red 170 has largely replaced it:



It has a similar shade to CI Pigment Red 112, but is available in a strong bluish shade or in a yellower, opaque form. The extra carbonamide group imparts much higher solvent resistance; it can be used in combination with higher quality pigments, for automotive finishes, especially in its opaque form.

It is possible to add another carbonamide group, e.g. CI Pigment Orange 38:



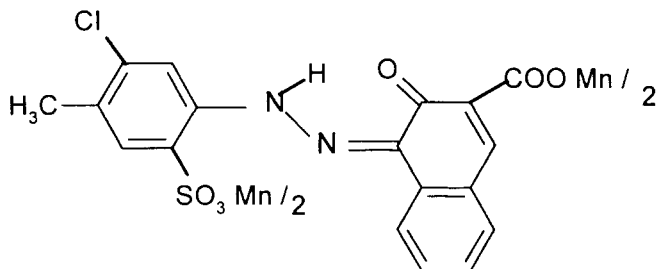
This pigment finds little use in paint as it only has moderate light fastness, but is worthy of inclusion to illustrate the effect of the carbonamide group, as this pigment can be used for the coloration of polymers such as PVC and polyolefins.

These pigments vary enormously in price, but usually offer the most economic colorations, providing their fastness properties are adequate.

3.12.6.6 Toner pigments

Colour Index — CI Pigment Red 48, 57, 60, 68 (an additional colon and number signifies the metal group). There are several other pigments of this type, but have little application in paint, usually due to poor light fastness.

Formula — CI Pigment Red 48:4:



One of the simplest ways of improving a coloured molecule's insolubility in organic solvents is to introduce a metal into the molecule. This can most readily be achieved by adding one or more acid groups to the molecule, then reacting this acid with an alkaline earth metal (or manganese) salt. The metal used has a significant effect on the shade of the pigment and on its fastness properties. This class of pigment is very important to the printing ink industry, where CI Pigment Red 57:1 is the normal standard for the magenta process colour used in three and four colour sets.

The base molecule can be simple β -naphthol azo molecules or β -naphthol azo molecules with a carboxylic acid on the naphthol (known as BONA toners, **B**eta **O**xy **N**apththoic **A**cid). As well as being very economic, they cover a wide range of the spectrum from yellow (although not very important) through red and magenta to violet. They have reasonably good solvent fastness, much better than similar pigments without the metal group, and several are very heat stable. Light fastness varies and partially depends on the metal, manganese giving the best results. Their biggest

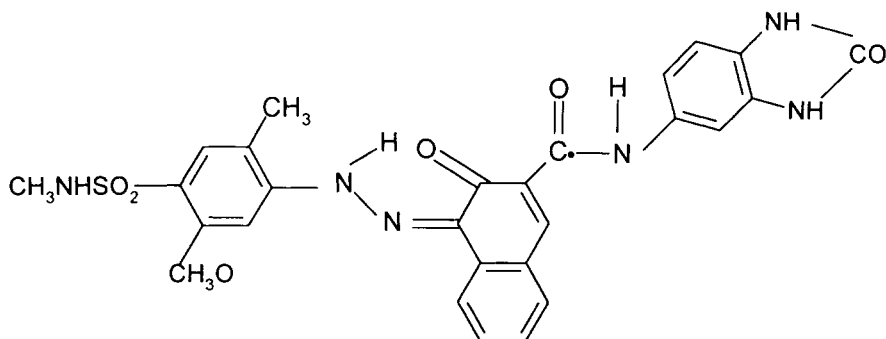
drawback is their poor resistance to acids and alkalis; even water can affect them. Poor chemical stability limits their use in paints to industrial finishes where this property is not necessary.

There have been some developments in recent years, where the more complex Naphthol AS® molecules have had an acid group added. These pigments provide economic, heat-stable pigments for polymer coloration.

3.12.6.7 Benzimidazolone red and brown pigments

Colour Index — CI Pigment Red 171, 175, 176, 185, 208, Violet 32, Brown 25.

Formula — as represented by CI Pigment Red 185:

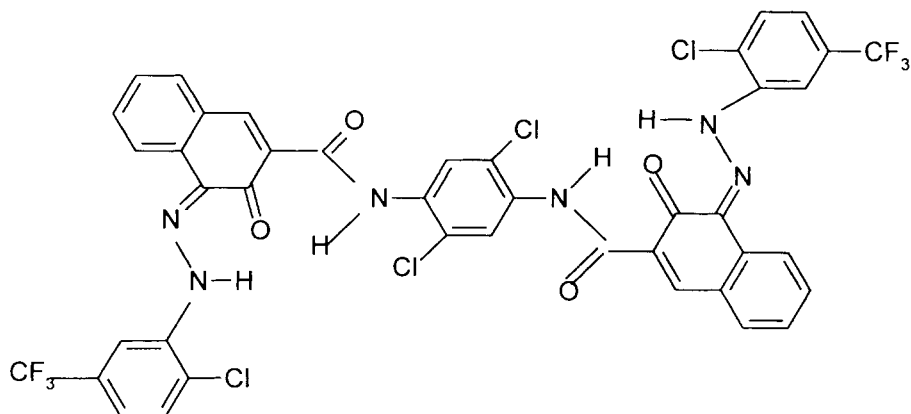


The introduction of the carbonamide groups via the benzimidazolone group provides this range of pigments with their high solvent resistance and good heat stability. However, several of the pigments in the series are rather dull in shade and others, although they have good light fastness, do not meet the highest requirements. Their main application tends to be in plastics, but CI Pigment Red 171, Red 175 and Brown 25 are used in metallic automotive and vehicle refinishing paints. They are relatively economic when compared with other high-quality pigments.

3.12.6.8 Disazo condensation pigments

Colour Index — CI Pigment Orange 31, Red 144, 166, 214, 220, 221, 242, Brown 23.

Formula — as represented by CI Pigment Red 242:



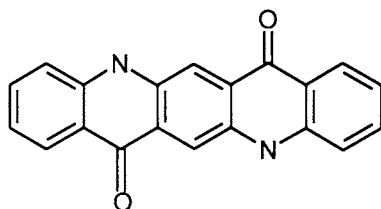
As in the yellow and orange series, the red disazo condensation pigments are characterized by good solvent resistance and excellent heat stability, because of the linking of two azo red molecules to a diamine by means of carbonamide groups. They range in shade from scarlet through bluish red to violet and brown. Their main use is in plastics, but several are used for industrial and occasionally vehicle refinishing paints and as the basis of tinting systems. They generally have bright shades.

CI Pigment Brown 23 is used for OEM automotive metallics and finds wide use in PVC coil coatings. Their price generally lies between the benzimidazolone pigments and the more complex polycyclic pigments described later.

3.12.6.9 Quinacridone pigments

Colour Index — CI Pigment Red 122, 192, 202, 207, 209, Violet 19.

Formula — as represented by CI Pigment Violet 19:



Few classes of pigment have seen the sustained growth shown by the quinacridone series. They are distinguished by their bright colours, which have excellent solvent stability, heat stability, chemical resistance, and high light fastness.

CI Pigment Violet 19 is unsubstituted and is available in two crystal forms, one having a bright mid-red shade and the other being red violet. A third crystal form is known, but it does not have favourable pigmentary properties, due to the crystal shape not allowing the formation of secondary bonds.

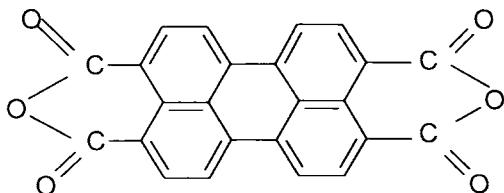
They are relatively expensive, but find application in most pigment using industries. In paint they are used in automotive OEM, vehicle refinishing, high-quality industrial finishes, and decorative tinting systems. Their high fastness properties are attributed to the formation of secondary bonds between the molecules. This can only exist in the β and γ crystal modifications.

There is a similar class of pigments known as 'quinacridone quinone' pigments, which are less bright and have poorer fastness properties, but are little used outside the USA.

3.12.6.10 Perylene pigments

Colour Index — CI Pigment Red 123, 149, 178, 179, 190, 224, Violet 29, Black 31, 32.

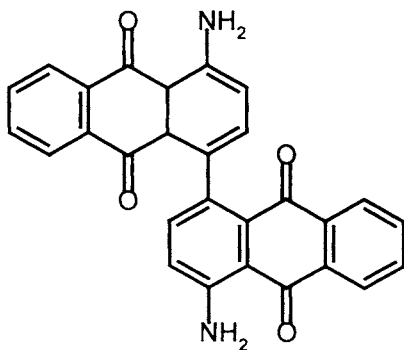
Formula — as represented by CI Pigment Red 224:



Although discovered in the early years of the twentieth century and used as vat dyes, these colorants were not developed as commercial pigments for nearly half a century. They have excellent solvent resistance, heat stability and light fastness. Chemical resistance is normally excellent but CI Pigment Red 224 lacks alkali stability. Some grades are available in both high-opacity and high-strength forms. The transparent forms are used for OEM automotive finishes whereas the opaque forms are used in full shades, where their high cost can be justified by their excellent properties.

3.12.6.11 Anthraquinone

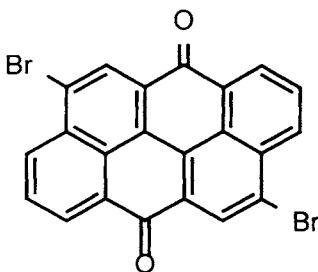
Colour Index — CI Pigment Red 177.



This pigment has a unique bright, strong shade that is frequently used in automotive metallics, often in combination with transparent iron oxides, and formerly in solid shades with molybdate reds. It has good resistance to solvents and heat stability. Its light fastness is good, but only attains the standards required by automotive finishes when used in combination with pigments that improve performance. In paler white reductions, light fastness rapidly declines. It is relatively expensive.

3.12.6.12 Dibromanthrone

Colour Index — CI Pigment Red 168.

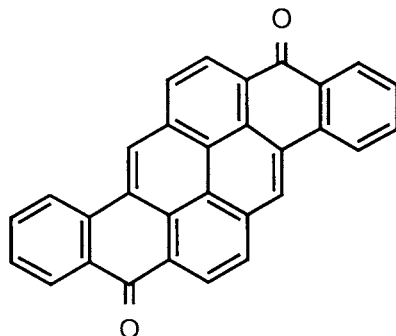


This pigment is also a vat dye. It has a bright scarlet shade with very good resistance to solvents. Its heat stability is sufficient for most paint systems and it has exceptionally good light fastness. Its high price limits its use mainly to automotive OEM and vehicle refinishing paints, coil coatings, and occasionally to tinting systems, where even in pale tints it retains excellent light fastness.

3.12.6.13 *Pyranthrone red*

Colour Index — CI Pigment Red 216, 226, Orange 51.

Formula — as represented by CI Pigment Red 216:

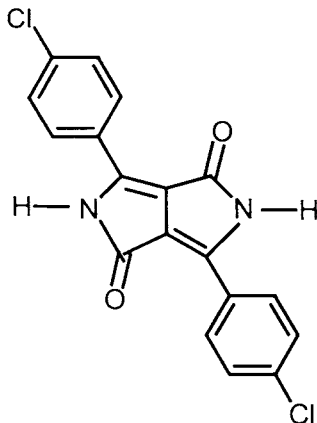


These pigments are chemically related to flavanthrone and are mainly used for their transparency. They have a rather dull shade (except CI Pigment Orange 51) and good fastness to solvents, but the heat stability of CI Pigment 216 is somewhat limited. Good, light fastness deteriorates rapidly in combinations with titanium dioxide.

3.12.6.14 *Diketopyrrolo-pyrrole pigments (DPP)*

Colour Index — CI Pigment Red 254, 255, 264, 270, 272, Orange 71, 73.

Formula — as represented by CI Pigment Red 254:



These pigments have only recently been introduced, but immediately found application on account of their bright shade, good opacity, excellent heat stability and resistance to solvents. They meet the requirements of the most demanding applications, including automotive OEM, although often used in combination with other more economic pigments, especially high opacity grades of CI Pigment Red 170 and CI Pigment 48:4 (2B manganese toner).

3.12.7 Violet pigments

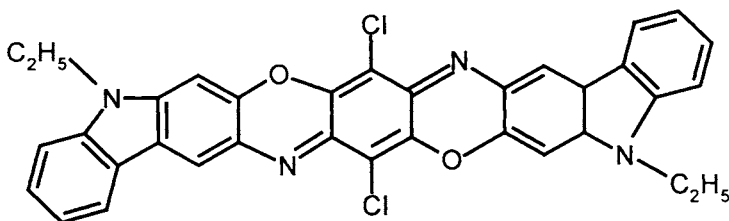
Although violet paints are not often seen, violet pigments attract considerable usage, because they bridge the gap between red and blue. If one mixes blue and red,

the result is a dull maroon colour or even brown, whereas a violet pigment allows one to blue off red paints and redden off blue paints, without going dull. Violet can also be used for tinting white to counter the basic yellow tint of titanium dioxide. For the paint industry, one chemical type dominates—dioxazine violet.

3.12.7.1 Dioxazine violet

Colour Index — CI Pigment Violet 23, 37.

Formula — As represented by CI Pigment Violet 23:



These pigments are widely used in a variety of paint systems from water-based emulsions to automotive OEM and coil coatings. They possess excellent solvent fastness and heat stability, and very good light fastness. Although relatively expensive, their very high strength makes them reasonably economic for most applications. CI Pigment Violet 23 (carbazole violet) is more transparent and bluer than CI Pigment Violet 37, and is therefore preferred for metallic paints.

Their very small particle size makes them vulnerable to flocculation and can also lead to plate out in some powder coating systems.

3.12.8 Blue pigments

There are relatively few blue pigments, because one chemical type totally dominates this part of the spectrum. Phthalocyanine provides us with what must be considered almost the ideal pigment. There are a large number of manufacturers, many just specializing in phthalocyanines. In the paint industry, a vat pigment, indanthrone, is used for some special high quality applications, and two inorganic pigments, ultramarine and prussian blue are occasionally used. The printing ink industry does use some cationic toners (phospho tungsto molybdic acid, ferrocyanide and alkali blue pigments), but their poor solvent and chemical resistance coupled with poor light fastness means they have virtually no use in paint.

Inorganic:

- Prussian blue
- Ultramarine
- Cobalt blue

Organic:

- Copper and copper-free phthalocyanine
- Indanthrone

3.12.8.1 Prussian blue

Colour Index — CI Pigment Blue 27.

Formula — $\text{FeK}_4\text{Fe}(\text{CN})_6$ ferric potassium ferrocyanide, or the ammonium salt.

This pigment is principally used in printing inks, where it is called milori or iron blue. It gives an intense, strong colour that improves the jetness of black inks. It is solvent-fast and has reasonably good heat stability. However, it has poor alkali stability, making it unsuitable for colouring emulsion paints that are to be applied to plaster.

3.12.8.2 Ultramarine

Colour Index — CI Pigment Blue 29, Violet 15.

Formula — approximately $\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$.

Ultramarine is a synthetic form of lapis lazuli, a naturally occurring mineral, prized by medieval artists. It is used for its brilliant colour and clean shade, ranging from pink, through violet to green. It has excellent heat stability and solvent resistance. It has good light fastness and alkali stability, but is unstable to acids, making it unsuitable for paints being used in industrial atmospheres.

3.12.8.3 Cobalt blue/green

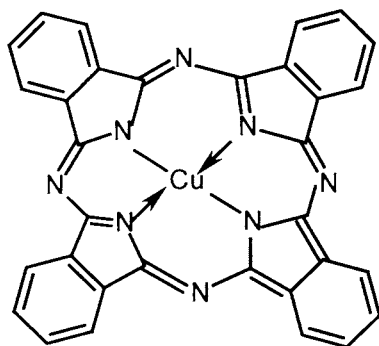
Colour Index — CI Pigment Blue 36, Green 50.

Formula — $\text{Co}(\text{Al}, \text{Cr})_2\text{O}_4$ (blue), $(\text{Co}, \text{Ni}, \text{Zn})_2\text{TiO}_4$.

These colorants belong to the 'complex inorganic colour pigment'. They are highly heat stable, have excellent solvent fastness, chemical stability, and light fastness. They can be used for the most demanding applications, but they are most used in very pale shades where high light fastness is required.

3.12.8.4 Copper phthalocyanine

Colour Index — CI Pigment Blue 15, 15:1, 15:2, 15:3, 15:4, 15:6 and Blue 16.



The phthalocyanine molecule, complexed around iron, was discovered in 1928 by Scottish Dyes (later to become ICI and now Zeneca); however, commercial grades were not introduced until around 1940. In many ways they are ideal pigments, having high colour strength, excellent heat stability, and good light fastness. Most grades have excellent resistance to solvents. While the chemical synthesis of phthalocyanine is relatively easy, converting it into a commercial product is more difficult.

The pigment is polymorphic, existing in at least five crystal forms, but only three are commercially produced:

- α phthalocyanine, reddish shade but unstable to aromatic hydrocarbons;
- β phthalocyanine, greenish blue;
- γ phthalocyanine does not exist as a commercial pigment;
- δ phthalocyanine does not exist as a commercial pigment;
- ϵ phthalocyanine, slightly redder than the α form.

The α modification (CI Pigment Blue 15) has a reddish shade but is its unstable form and when used in aromatic solvents converts to the β grade. It can be stabilized (CI Pigment Blue 15:1) by slightly chlorinating (about half an atom of chlorine per phthalocyanine molecule). In doing so one also makes the pigment greener and tinctorially weaker. It can be treated to make it stable to flocculation (CI Pigment Blue 15:2).

CI Pigment Blue 15:3 is the β modification and has a greener, purer shade thus giving the cyan standard for three and four colour printing inks. If treated to make it flocculation stable, it is designated CI Pigment Blue 15:4.

CI Pigment Blue 15:6 is the δ modification, but is considered something of a speciality and little used. CI Pigment Blue 16 is the metal-free grade. It is a β crystal modification and possesses high transparency and even slightly superior durability, and was widely used for metallic shades, where it gave attractive flip tones. However, its use has declined in recent years, largely because of improved grades of the conventional β modification. In addition there is also a trichlorinated phthalocyanine which is also used for metallics and a grade which replaces the copper with an aluminium compound, in order to reduce copper content.

In spite of their excellent performance characteristics, copper phthalocyanine pigments are among the cheapest organic pigments on the market, their very high tinctorial strength making them very economic in use. Many companies manufacture copper phthalocyanine pigments.

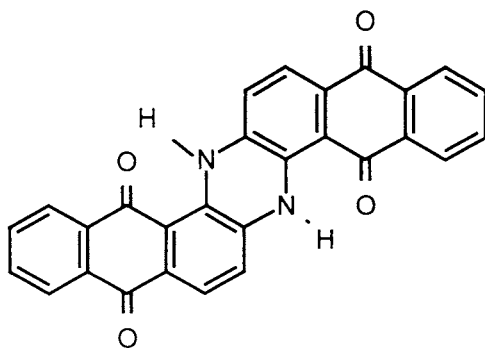
Copper phthalocyanine pigments are quite transparent and can be used in solid, reduced, and metallic automotive coatings. Because the primary particles of phthalocyanine are so small, they have a tendency to flocculate and the loss of colour strength in such a tinctorially strong pigment is very noticeable. The flocculation stable grades are prepared by coating the particles with products that will prevent the particles from re-aggregating. A number of products can be used:

- sulphonated phthalocyanine;
- long chain amine derivatives of sulphonated phthalocyanine;
- aluminium benzoate;
- acidic resins, e.g. rosin;
- chloromethyl derivatives of phthalocyanine.

These stabilized phthalocyanines often show a greater purity of shade, easier dispersibility and better gloss than untreated grades, but are significantly more expensive.

3.12.8.5 Indanthrone

Colour Index — CI Pigment Blue 60.



Indanthrone blue is also a vat dye (CI Vat Blue 4). As a pigment it is polymorphic, with four known crystal forms, but the α modification provides us with the most stable pigment. It has a deep reddish blue shade, possessing much better stability to flocculation and even higher durability than phthalocyanine blues. It has excellent chemical and solvent resistance, very good heat stability and is highly transparent. It is used in high-performance paints, including automotive OEM finishes, especially pale shades and metallics. A chlorinated version (CI Pigment Blue 64) was used, but there are currently no known manufacturers.

3.12.9 Green pigments

As in the blue part of the spectrum, copper phthalocyanine pigments dominate the green sector. In practice, greens are often obtained by mixing yellows and blues, the brightness required and economics determining the best approach. Inorganic pigments play a relatively unimportant role.

Inorganics:

- Chrome green (Brunswick green)
- Chromium oxide
- Hydrated chromium oxide

Organic:

- Halogenated copper phthalocyanine

3.12.9.1 Chrome green (Brunswick green)

Colour Index — CI Pigment Green 15.

Formula — A co-precipitate or dry blend of chrome yellow and Prussian blue,
 $\text{PbCrO}_4 \cdot \text{PbSO}_4 \cdot \text{FeNH}_4\text{Fe}(\text{CN})_6$.

These pigments inherit the strengths and weaknesses of the parent pigments. They have an additional disadvantage because they wet out at different rates, leading to floating and flooding. Some grades substitute phthalocyanine blue for Prussian blue.

3.12.9.2 Chromium oxide green

Colour Index — CI Pigment Green 17.

Formula — Cr_2O_3 chromium sesquioxide.

This pigment has a dull shade, good opacity but low tinctorial strength. It has excellent heat stability, excellent resistance to solvents and chemicals, and excellent light fastness. It should not be confused with other 'chrome' pigments, as the chrome is in the trivalent form, which is inert and appears to be free from toxicological and adverse environmental effects. It is a very hard abrasive pigment and can cause excessive wear on dispersion equipment.

It is used mainly on account of its excellent fastness properties and its ability to reflect infrared radiation, allowing its use in camouflage coatings.

3.12.9.3 Hydrated chromium oxide

Colour Index — CI Pigment Green 18.

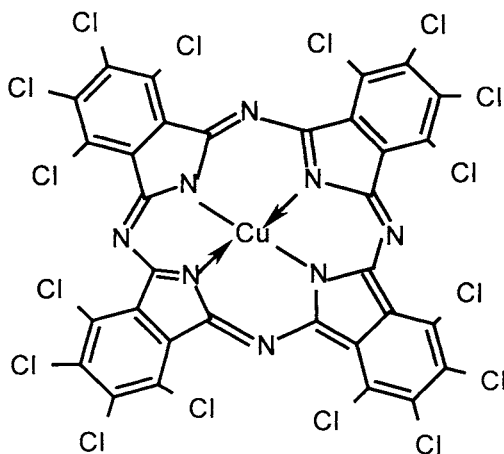
Formula — hydrated chromium oxide, $\text{Cr}_2\text{O}(\text{OH})_4$.

This pigment is chemically similar to chromium oxide, but the water of hydration leads to a much brighter and transparent pigment. Its light fastness is excellent but it is less heat stable and has slightly less stability to acids.

3.12.9.4 Phthalocyanine green

Colour Index — CI Pigment Green 7, 36.

Formula — As represented by CI Pigment Green 7:



The colour range of phthalocyanine green is dependent on the degree and type of halogenation. CI Pigment Green 7 has a bluish green tone, with excellent properties, even better than the blue grades. It has excellent solvent and chemical resistance, high heat stability, and excellent light fastness. It has a high tinctorial strength, and while the early products and less sophisticated grades are very difficult to disperse and have a tendency to flocculate, most modern commercial products are reasonably easy to disperse and are less prone to flocculation. It is normally transparent and therefore this pigment can be used for virtually all paint systems including all types of automotive OEM finishes, including metallics, powder coatings, industrial finishes and decorative paints.

CI Pigment Green 36 is chloro-brominated and has similar properties, but is much yellower in shade and is very bright. Its significantly higher price and much lower tinctorial strength tend to limit its application to high-quality finishes.

3.12.10 Special effect pigments

Certain pigments are used to give special effects, rather than for the colour. The best-known products to the paint technologists are the pigments used in metallic and flamboyant finishes to give a sparkle effect. They can give this effect in two quite different ways, as represented by:

- aluminium flake pigments;
- pearlescent pigments.

3.12.10.1 Aluminium flake pigments

Colour Index — CI Pigment Metal 1.

Formula — aluminium (Al).

There are two types of aluminium pigment:

- leafing;
- non-leafing.

The classification is based more on the effect they give, rather than any fundamental difference in the aluminium. These effects are achieved by the use of surface-active agents used on the aluminium.

Adding stearic acid to the aluminium particles produces the leafing types, which give the appearance of a continuous film of metal, almost mirror-like. The aluminium particles align themselves on the surface during the paint's drying process. They can be used with transparent pigments to produce coloured effects, but the aluminium must be added after the dispersion process as over-dispersion damages their stearate coating. Because the pigment aligns itself as plates, it prevents water penetrating the paint film, and provides corrosion protection to the surface of the substrate.

The non-leafing types remain within the film, producing a 'polychromatic' effect, so called because the colour looks different depending on the angle of view and the angle of the incident light. The effect is often described as 'flop' and is usually associated with automotive metallic paints and hammer finishes. They are often coloured with transparent or semi-transparent pigments. Lauric or oleic acid is used on the surface during the production of the pigment.

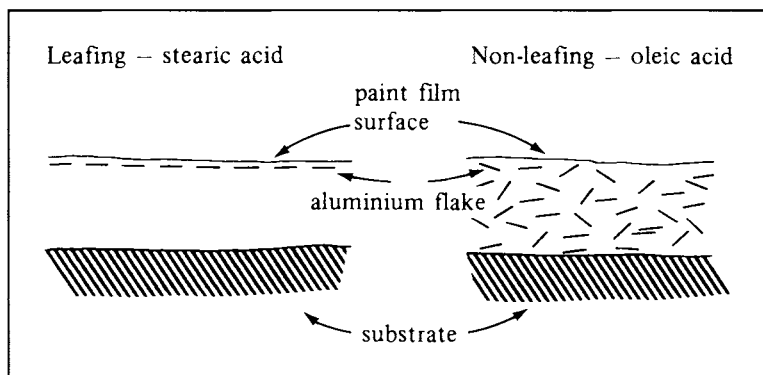


Fig. 3.5 — Aluminium flake pigments in a paint film (cross-section).

Aluminium pigments are produced by ball milling finely divided aluminium powder, down to a particle size of anything between $1.2\mu\text{m}$ and $80\mu\text{m}$, in the presence of the appropriate stearate. Filtering and sieving follow to provide the various grades supplied to the paint industry.

Although aluminium shows no acute toxicity, care has to be taken when using it in acidic media, as both the leafing properties and sheen can be adversely affected, and hydrogen gas can be evolved. The stearic acid in leafing grades can also react with naphthanates and rosinsates used as driers, which results in the deleafing of the aluminium. Most commercial grades are available as dust-free pastes with white spirit or other hydrocarbon solvents, as aluminium powder can cause explosive mixtures in air.

3.12.10.2 *Pearlescent pigments*

Colour Index — Not designated.

Formula — Principally mica coated with metal compounds, especially titanium dioxide.

A number of natural products and minerals give a pearlescent effect, including:

- natural platelets composed of guanine with hypoxanthine, commonly called 'fish silver', as they are derived from the scales of fish;
- basic lead carbonate, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$;
- bismuth oxychloride, BiOCl ;
- mica flakes coated with titanium, iron or chrome oxides.

The pigment particles are transparent, thin platelets of a high refractive index, which partially reflect and partially transmit incident light. These platelets can stack up in layers, creating a third dimension and giving rise to the typical pearlescent lustre. The iridescent or 'interference' pigments are those where at a particular optical thickness, interference occurs between the partly reflected and partly transmitted light rays, cancelling out some wavelengths and reinforcing others, giving rise to a play of subtle colours or 'iridescence' as well as the pearly lustre.

Unlike normal pigments, where colours are subtractive (i.e. blue and yellow gives green), mixing interference pigments leads to 'additive' colour mixing (i.e. blue and yellow produces white). The smaller particles give a satin effect, whereas coarser particles produce a sparkle, similar to aluminium.

Pearlescent pigments of the titanium-coated mica type are now widely used in automotive finishes, usually in combination with highly transparent pigments to produce brilliant effects. The titanium dioxide used in the pigment should be of the rutile type, otherwise durability of the paint film can be adversely affected.

3.12.11 **Extender pigments**

As the name implies, the main purpose of such pigments is simply to 'extend' the more expensive white and coloured pigments, so cheapening the paint formulation. However, the use of such pigments contributes much more to the paint's properties so careful selection of the type and quantity can affect such features as:

- flow properties (rheology);
- stability to sedimentation (anti-settling);
- film strength.

Most extenders are white in colour and have a refractive index close to those of commonly used binders (1.4–1.7). Hence, unlike titanium dioxide, which has a refractive index of around 2.7, they give relatively little opacifying effect. Most are naturally occurring, but may require purifying. Others are produced synthetically.

- Calcium carbonate (synthetic and natural)
- Aluminium silicate (china clay)
- Magnesium silicate (talc)
- Barium sulphate (natural — barytes; synthetic — blanc fixe)
- Silica

3.12.11.1 *Calcium carbonate (chalk, whiting, Paris white)*

Colour Index — CI Pigment White 18.

Formula— CaCO_3 .

Naturally, calcium carbonate is obtained from chalk or limestone. It is often known as whiting and is obtained in its natural state with a purity of around 96%.

Synthetic grades are often known as ‘precipitated calcium carbonate’, being produced by calcining limestone, followed by slaking and purifying. The calcium hydroxide suspension is then converted to the carbonate by passing carbon dioxide through the solution. As such, they are often made by using by-products of other industrial processes and from water softening processes.

They are cheap and are widely used in water- and solvent-based paints, for interior and exterior decoration. Their low oil absorption allows them to be used at relatively high levels imparting some structure to the wet paint, improving the stability to sedimentation of other heavier pigments and imparting sag resistance in paint films. Calcium carbonate reacts with acids, but in other respects is stable.

3.12.11.2 *Aluminium silicate (china clay, kaolin, calcined clay)*

Colour Index — CI Pigment White 19.

Formula — $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

China clay is inert and has a good colour. It occurs naturally through the breakdown of granite, along with silica and mica. It exists as plate-like particles, with a particle size between 0.5 and 50 μm . It imparts some thixotropy in paints and is used as a cheap flattening agent and produces a structure that improves the suspension of other pigments. A major use is in water-borne decorative paints.

Fine particle size grades (between 0.2 and 0.4 μm), especially the calcined versions, can be used partially to replace the more expensive opaque pigments such as titanium dioxide, while retaining some opacity.

3.12.11.3 *Magnesium silicate (talc, French chalk, asbestine)*

Colour Index — CI Pigment White 26.

Formula — typically hydrated magnesium silicate $3\text{Mg} \cdot 0.4 \text{SiO}_2 \cdot \text{H}_2\text{O}$.

The term ‘talc’ covers a number of minerals with varying chemical composition, but based on magnesia and silica, with calcium and aluminium as impurities. Rocks containing talc are crushed and then milled to give lamella or fibrous extender pigments, which are then classified.

Talc is inert and hydrophobic. Its plate-like form helps to prevent pigment settlement in the wet paint, improves flow behaviour, especially when brushing out and

provides some resistance to humidity. It also enhances the sanding properties of paint films. It is used in both solvent- and water-based decorative paints as well as in undercoats and industrial finishes.

3.12.11.4 Barium sulphate (*natural — barytes; synthetic — blanc fixe*)

Colour Index — Barytes, CI Pigment White 22; blanc fixe, CI Pigment White 21.

Formula — BaSO_4 .

Barium sulphate is very inert, insoluble and stable to light and heat. The natural form is obtained as the mineral 'heavy spar'. After being crushed, washed and dried it is usually micronized, reducing its particle size from $25\mu\text{m}$ to $2\text{--}10\mu\text{m}$, thus aiding its dispersibility. The synthetic version is made by reacting available barium compounds with sulphuric acid or soluble sulphate salts, and has a finer texture than the natural grades, giving it a higher oil absorption.

Its refractive index (1.64) is higher than other extenders, which gives it some pigimentary properties. Its high density is also useful for paints sold by weight. It is used in primers, undercoats, and industrial finishes, where it hardens the film. Its high density leads to it having a tendency to settle. In spite of it being a barium salt, its insolubility ensures it is non-toxic.

3.12.11.5 Silica

Colour Index — CI Pigment White 27.

Formula — SiO_2 .

Silica is available from both natural and synthetic sources. Natural sources include:

- diatomaceous earth, e.g. kieselguhr, Celite®.
- 'amorphous' silica (actually cryptocrystalline).
- crystalline silica — quartz, can cause silicosis, and therefore a health hazard.

Diatomaceous earth such as Kieselguhr consists of soft siliceous remains of diatoms (a type of fossilised algae) deposited over long periods of time. The synthetic grades include precipitated silica with extremely small particle size, which can even be colloidal.

The finer grades of these extenders are used as matting agents, reducing the gloss of paint films. They improve intercoat adhesion and the sanding properties of the paint film.

3.12.12 Corrosion-inhibiting pigments

Corrosion is the destruction of metal by chemical attack, such as rusting of iron or tarnishing of copper. It requires:

- a thermodynamically unstable metal;
- an electrolytic conductor of ions;
- an electrical conductor;
- an electron acceptor.

Pigments can help prevent corrosion by:

- helping to provide a physical barrier to the passage of water and oxygen;
- being sacrificially destroyed as an anode, thus protecting the anodic sites that have become pitted;

- providing soluble passivating ions to protect the metal; or
- producing an insoluble film, which prevents active corrosion.

Traditionally the main corrosion-inhibiting pigments were:

- Red lead, CI Pigment Red 105
- Basic lead silicochromate, not listed
- Zinc chromate, CI Pigment Yellow 36
- Strontium chromate, CI Pigment Yellow 32
- Calcium, strontium and zinc molybdate, not listed
- Calcium plumbate, CI Pigment Brown 10
- Zinc phosphate, CI Pigment White 32
- Zinc dust, CI Pigment Metal 6
- Micaceous iron oxide, not listed

However, concerns regarding the toxicity of many of these pigments, mainly those containing lead or chrome VI have resulted in new approaches. The alternatives are less universal and need carefully selecting for the precise application required. So before choosing an anti-corrosive pigment it is absolutely essential to read the safety data and the technical information, in order to obtain optimum results.

3.12.12.1 *Red Lead*

Colour Index — CI Pigment Red 105.

Formula — Pb_3O_4 .

Red lead is mainly used in primers for metal protection, where it reacts with the acidic groups in the resin to give lead soaps that passivate iron and steel surfaces.

3.12.12.2 *Basic lead silico chromate (Oncur)*

Colour Index — core SiO_2 coating $\text{PbSiO}_3 \cdot 3\text{PbO} \cdot \text{PbCrO}_4 \cdot \text{PbO}$.

The lead silicate–lead chromate coating is firmly bound to the silica core, producing a pigment that is easy to disperse and gives excellent metal protection in structural steel and automotive paints. Finer grades can be used in electrocoat paints.

3.12.12.3 *Zinc chromates: basic zinc chromate, zinc tetroxy chromate*

Colour Index — CI Pigment Yellow 36.

Formula — ZnCrO_4 , $\text{K}_2\text{CrO}_4 \cdot 3\text{ZnCrO}_4 \cdot \text{Zn}(\text{OH})_2$, $\text{ZnCrO}_4 \cdot 4\text{Zn}(\text{OH})_2$.

These pigments liberate chromate ions, which passivate metal surfaces, producing a protective film at the anodes, thus inhibiting the anodic reaction. They were used for iron, steel, and aluminium protection, but their physiological properties make them unsuitable.

3.12.12.4 *Calcium, strontium, and zinc molybdates*

Colour Index — not listed.

Formula — CaMoO_4 , SrMoO_4 , ZnMoO_4 .

These three pigments, all of which are white, passivate the anode. Their use has grown considerably in recent years on account of their more favourable physiological properties.

3.12.12.5 *Calcium plumbate*

Colour Index — CI Pigment Brown 10.

Formula — Ca_2PbO_4 .

This pigment is a strong oxidizing agent and also reacts with the acid groups in binders with fatty acid groups such as linseed oil; to give lead and calcium soaps. This promotes adhesion in the paint film and confers toughness. The corrosion-inhibiting effects are due to the pigment's ability to oxidize soluble iron compounds formed in anodic areas, which can then form an insoluble film of iron compounds at the anode, thus neutralizing that element of the 'corrosion cell' and preventing further corrosion. Meanwhile calcium carbonate is generated at the cathodic region of the 'corrosion cell'.

3.12.12.6 *Zinc phosphate*

Colour Index — CI Pigment White 32.

Formula — $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

More specifically, it is zinc orthophosphate dihydrate that has the superior corrosion resistance properties. While this pigment was recognized as conferring good durability, excellent intercoat adhesion, and good flow properties in paint systems, its anti-corrosive properties were not fully understood. It is now recognized that in industrial atmospheres it reacts with ammonium sulphate to form complex hetero acids, which inhibit corrosion. Although it is a white powder, the pigment has very low reducing power.

A number of modifications are also offered, including aluminium zinc phosphate, zinc molybdenum phosphate and zinc silicophosphate hydrate. Zinc hydroxyphosphate also plays a role.

3.12.12.7 *Zinc dust*

Colour Index — CI Pigment Metal 6 and CI Pigment Black 16.

Formula — Zn .

Zinc dust is a fine bluish grey powder that reacts with oils to produce zinc soaps and with alkalis to give zincates. Corrosion resistance is imparted by a sacrificial chemical reaction of the pigment rather than the steel substrate. It also absorbs UV radiation, thus protecting the film formers in exterior coatings. Zinc-rich primers can be used for steel construction even where there will be subsequent welding.

The search to find more physiologically acceptable corrosion-inhibiting pigments has uncovered a number of possible inhibitors. Zinc, calcium, and strontium molybdates have been described, as has zinc phosphate. Other phosphates include basic molybdenum phosphate, aluminium triphosphate, and various polyphosphates. Borates can also be used, such as barium metaborate and zinc borate. Silicates such as calcium borosilicate, calcium barium phosphosilicate, calcium strontium phosphosilicate, and calcium strontium zinc phosphosilicate are all offered.

Mention has been made of **micaceous iron oxide** and aluminium acting as a barrier pigment; steel flake can offer similar protection.

As knowledge on the toxicity properties of these types of pigments is constantly developing, it is essential to keep up to date with published safety data. It is also necessary to give more attention to formulation details than was perhaps necessary with traditional pigments, as economics becomes a much more critical factor in the

consideration of performance. The pigment loading and the pigment volume concentration that give optimum results are likely to have a much smaller 'window' than has previously been the case.

References

- [1] DCMA, *Amer Inkmaker*, **June** (1989).
- [2] ETAD/BCMA/VDMI/EPSOM, *Safe Handling of Pigments*, European Edition (1995).
- [3] SANDERS J D, *Pigments for Inkmakers*, SITA Technology, London p. 19 (1989).
- [4] HERBST W & HUNGER K, *Industrial Organic Pigments*, VCH, Weinheim (1993).
- [5] JONES F, in *Pigments — An Introduction to Their Physical Chemistry*, Patterson D, Editor, Elsevier (1967), pp. 12–15.
- [6] FEITKNECHT W, in *Pigments — An Introduction to Their Physical Chemistry*, Patterson D, Editor, Elsevier (1967), pp. 1–25.
- [7] PATTERSON D, in *Pigments — An Introduction to Their Physical Chemistry*, Patterson D, Editor, Elsevier (1967), pp. 50–65.
- [8] HOECHST, BP 1455653 Disazo Pigment (1974).
- [9] BALFOUR J G, *J Oil Colour Chem Assoc JOCCA*, **June** (1990).
- [10] SMITH J L, *Amer Ink Maker*, **September** (1994), pp. 41–48.
- [11] *Colour Index International*, Third edition, Society of Dyers and Colourists American Association of Textile Chemists and Colorists (1971).
- [12] *Colour Index International*, Third edition, *Pigment and Solvent Dyes*, Society of Dyers and Colourists American Association of Textile Chemists and Colorists (1982, updated 1987, 1997).
- [13] CHRISTIE R, *PIGMENTS*, OCCA, pp. 1–3.
- [14] WHITAKER A, *Z Kristallogr* **147** 99–112 (1978).
- [15] WHITAKER A, *J Soc Dyers and Colourists* **94** 431–435 (1978).
- [16] WHITAKER A, *J Soc Dyers and Colourists* **104** 294–300 (1988).
- [17] SAPPOK R, *J Oil Colour Chem Assoc* **61** 299–308 (1978).
- [18] ALLEN T, in *Pigments — An Introduction to Their Physical Chemistry*, Patterson D, Editor, Elsevier (1967), pp. 102–133.
- [19] WASHINGTON C, *Particle size analysis — Pharmaceuticals and other industries. Theory and Practice*, Ellis Horwood (1992).
- [20] BRUNAUE R, EMMET P H, and TELLER E, *J Amer Chem Soc*, **60** 309 (1938).
- [21] HERBST W, *The Dispersing of Pigment, Farbe u Lack*, **76** (12) 1190–1208 (1970).
- [22] BERG I, in *Principles of Paint Formulation*, Woodbridge R, Editor, Blackie, Glasgow (1991).
- [23] ROTHE U *et al*, *Paint Colour J*, **182** S10–S16 (1992).
- [24] FULLER C W, in *Pigment Handbook*, Patton T C, Editor, John Wiley & Sons, New York, pp. 333–347 (1987).
- [25] KUHNER G, *What is Carbon Black?*, Degussa, Frankfurt, PT 17-15-3-0992 Be.
- [26] CPMA, *Safe Handling of Color Pigments*, Color Pigments Manufacturers Association, Alexandria, USA (1993).
- [27] STEIG F, *Principles of Paint Formulation*, Woodbridge R, Blackie, Glasgow (1991).
- [28] VALANTIN H & SCHALLER K H, *Human Biological Monitoring of Industrial Chemicals*, vol. 3, Titanium Commission of the European Community EUR 6609 (1980).