

CHAPTER 2

Organic and inorganic pigments; solvent dyes

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2.1 PIGMENTS

2.1.1 General introduction – what are pigments?

The word ‘colorant’ is defined in dictionaries as ‘a substance used for colouring’ and it can therefore be used to describe both dyes and pigments. Since this chapter is concerned only with pigments it is necessary to find a criterion for deciding whether a given colorant should be treated as a pigment or a dye. In practice this is not as simple as it might seem. One widely used criterion is that of the solubility of the colorant in the material which it is being used to colour. If it is insoluble, it is a pigment; if soluble, it is a dye.

The criterion of solubility is insufficient in itself, however. The same colorant can sometimes be a dye and, in other applications, a pigment. Vat dyes are an example of this. They were originally developed as dyes for textiles, but later were prepared in a different physical form for use as pigments. Indeed, it may be argued that since vat dyes are water-insoluble and to get them to diffuse into fibres they must first be reduced, they should not be considered as dyes at all, but as pigments. Again, the aqueous solubility of many disperse dyes is so low that various devices have to be used to induce them to diffuse into polyester fibres. From all of this, it is fair to say that there is no infallible simple criterion for deciding whether a colorant is a dye or a pigment. It is always necessary to take into account the actual use to which the colorant is being put.

A further, and most important, difference between pigments and dyes is that pigments are used as colorants in the physical form in which they are manufactured. Here, physical form means both the crystal structure and the particle size distribution of the pigment. The physical form of dyes is becoming of increasing importance as methods of handling them become more automated. In most dyeing processes, however, the dyes are first dissolved in water and their physical form is thereby destroyed. Thus physical form is not generally of such overriding importance as it is in the case of pigments.

Because of the requirements of insolubility in water, in organic solvents and in the medium that it is being used to colour, the application processes for using pigments are quite different from those for dyes. Coloration with pigments is essentially a process of dispersion of solid particles of the pigment in a semi-solid medium.

Entire technologies are involved in each of the three largest applications of pigments, which are as colorants in paints, plastics and printing inks [1]. Each of these media is composed mainly of organic constituents and the broad general rule that ‘like dissolves in like’ gives rise to considerable technical problems in some cases, particularly where entirely covalent organic pigments are being used. However, since some coloured pigments are

inorganic, as are all white pigments, many problems of migration and colour bleeding can be solved by changing from organic to inorganic pigments.

The chemical nature of most organic pigments is closely similar to that of the synthetic dyes that have been discovered during the past 150 years. In fact, with the exception of the phthalocyanines, almost every chemical class of pigments has been developed first for dyestuff use. There are some signs that this may not continue to be the case, with the development of some new organic pigments for specialised uses.

Finally, passing mention must be made of the two most important organic pigments in our world, both natural products. These are chlorophyll and haemoglobin, which are absolutely vital in the strict meaning of the word, but only chlorophyll has found a commercial use as a colorant in food preparation.

2.1.2 The background history of pigments

The discoveries of archaeologists indicate that the first pigments used by mankind, mainly to decorate both himself and his possessions, were the earth pigments. These are widely distributed throughout the world, are highly resistant to decomposition by heat, light and weathering, and indeed without these properties would not have survived through the centuries.

Earth pigments were probably first recognised simply because their colour stood out when hard lumps of rock were examined. Such rocks were broken up and the desirable coloured bits picked out. The coloured pigments were then ground to a fine powder and blown onto the painting surface using a hollow tube, or mixed with fatty materials to form a kind of crude paint that was applied with the fingers or a reed. The prehistoric cave paintings found in parts of Spain and France were made in this way.

Examples of such earth pigments are the bright red pigment vermilion (mercury sulphide), the yellow orpiment (arsenic trisulphide), the green malachite (basic copper carbonate) and the blue lapis lazuli (natural ultramarine). There are many natural sources of white pigments such as chalk and kaolin, while black pigments could be obtained as charcoal from incompletely burnt wood and as soot in smoke from burning oils. The *Colour Index* gives more examples, as do Kearton [2] and Skelton [3].

For many centuries, pigments have been derived from the colouring matters found occurring naturally in many plants and even in some animals. Examples are the red pigment madder and the blue indigo, both extracted from plants, cochineal and lac lake both from insects, the much-prized Tyrian purple derived from certain shellfish, logwood extracts ranging in colour from red to brown or black, depending on the precipitant, and finally sepia obtained from cuttlefish [4].

The methods used for making pigments from these and other natural dyes were more like recipes than scientific procedures and were probably derived from the work of alchemists and herbalists. The former spent their lives trying to prepare gold by dissolving all kinds of cheap substances in acids and then re-precipitating them (hence their discovery of many precipitants), while the latter sought to extract compounds of medicinal value from plants and some of their extracts must have included natural dyes.

Among the precipitants employed were tannic acid, tartar emetic, rosin soaps, fatty acid (stearic, oleic) soaps, sulphonated oils (Turkey red oil), 'earth lakes' (mixed natural silicates), phosphates, casein and arsenious acid. The fastness properties of these pigments

were relatively poor, both to water and to light. Furthermore, the colour of the pigments made by these methods largely depended on the particular precipitant or combination of precipitants used, a fact also exploited by medieval dyers to extend the range of colours that they could produce from the very limited number of natural dyes available to them. Many of the methods for making these pigments [5] are of historical interest only, except for a few which are mentioned later.

2.1.3 More recent developments

The industrial revolution brought about in the 19th century the rise of the chemical industry, which is such an important part of the world economy today. The discovery in the 1850s of the first synthetic dye by William Perkin and of the diazo reaction by Peter Griess started the search for other synthetic colorants, leading eventually to their almost complete market dominance. Many of what are now the largest international chemical companies began their activities in this area, later expanding into plastics and pharmaceuticals. For over a hundred years research aimed at synthesising new organic colorants was actively pursued. Patents were filed and new products appeared on the market. Thousands of new compounds were prepared and tested so that tens of new colorants, generally dyes, could be introduced commercially. Some of these were also tested for suitability as pigments, but few had all the properties required. Only the organic phthalocyanine and the inorganic titanium dioxide pigments have gone into large-scale production directly as pigments without being first used as dyes.

Certain commercial developments in the last twenty years or so have had important effects on the pattern of pigments production. One is the rapid growth of textile production in the Asia Pacific region and another is the development of automated dyeing methods, coupled with instrumental methods of colour measurement and of computerised colour recipe prediction.

Colorimetric prediction is equally applicable to pigment applications and this has directed attention to the possibility of rationalising the ranges of dyes and pigments needed. In theory, it should always be possible to match any shade by mixing three or four suitable colorants. This is probably one of the reasons for the reduction in the number of pigments commercially available. For example, the number of different yellow pigments allocated *Colour Index* numbers and listed in the 1982 edition of *Pigments and Solvent Dyes* was 166, but this had fallen to 121 in the 1997 edition. Of these, no less than 26 are inorganic, including 8 new entries. These are mixed oxides of various metals including titanium, zinc and vanadium intended for ceramic coloration and are mentioned later.

Other factors, such as the increasing use of pigments in textile printing, to such an extent that pigments now comprise nearly half of the colorants used for this purpose, means that the textile industry is an important market sector for pigments. The geographical shift of the textile industry has resulted in extensive reorganisation of some of the largest international companies that in the past have dominated the manufacture of colorants and some long-established commercial names have disappeared as a result.

Within the pigments industry itself, there has been a growing realisation that the physical state of pigments is of the greatest importance to pigment users. Most suppliers now offer several products based on the same chemical structure and the physical form in which it is supplied is chosen to suit the intended application. Thus, the 1997 edition of *Pigments and*

Solvent Dyes shows for each product, not only the application but also in which of eight different physical forms it is supplied. These forms are: powder, presscake, granule, chip or flake, liquid dispersion, paste, master batch, flush colour. Not all pigments are offered in all these physical forms, since for a particular application this may be neither possible nor necessary. To assist users, manufacturers frequently give a separate commercial name to each form in which they supply the pigment. With the exception of the powder form, this means that they will generally contain auxiliaries such as dispersing agents, chosen to assist in the process of incorporating them into the particular medium for which they are intended.

The increase in colour printing of newspapers and periodicals, in colour printing on various plastics for the packaging of foods sold in supermarkets, as well as the introduction of colour printers for use with personal computers, have all presented many technical problems in formulating coloured inks for these purposes. In *Pigments and Solvent Dyes*, CI Pigment Yellow 1, which has been in commercial production for a century, now has no less than 96 entries of commercial products based on it. This illustrates its widespread use in printing as well as in other applications, but also is a symptom of the tendency to contract the range of chemically different pigments in production.

Other recent developments, including fluorescent pigments, polymeric pigments and the problems which have arisen concerning health hazards from the use of benzidine-based intermediates in making certain pigments, are mentioned later in this chapter.

It should also be mentioned that the structural formulae of the azo pigments discussed in this chapter now take account of the investigations by Whitaker [6] into the crystal structures of these pigments. These have shown the importance of hydrogen bonding between the pigment molecules in the solid state. The molecular formulae and the chemical synthesis stages of the preparation of these pigments remain unchanged.

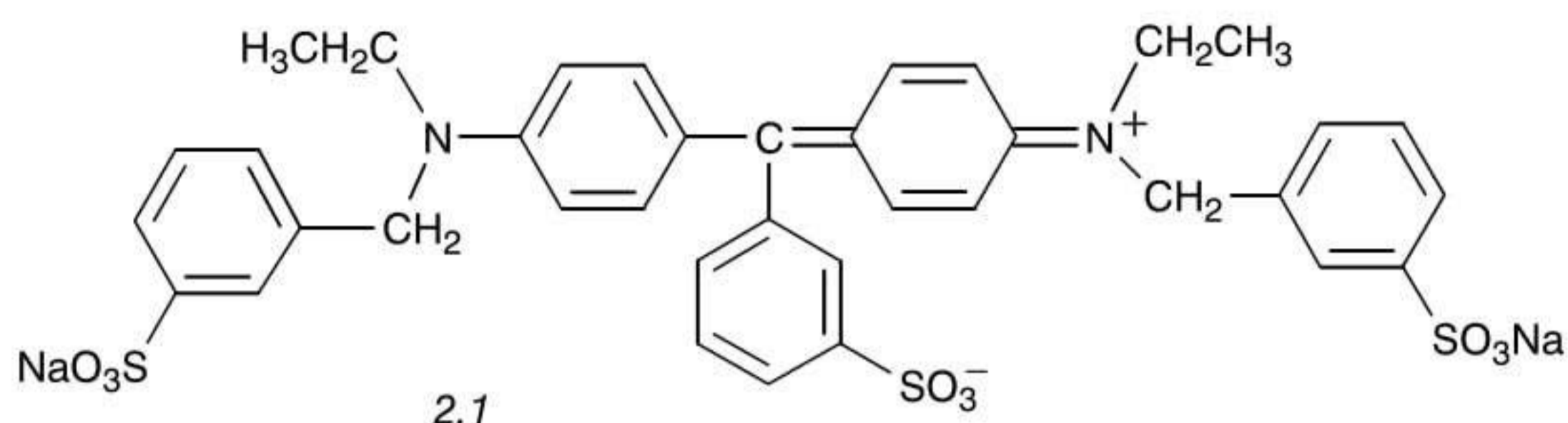
2.2 DYES CONVERTED INTO PIGMENTS

2.2.1 Dyes converted by precipitation on substrates – ‘lakes’

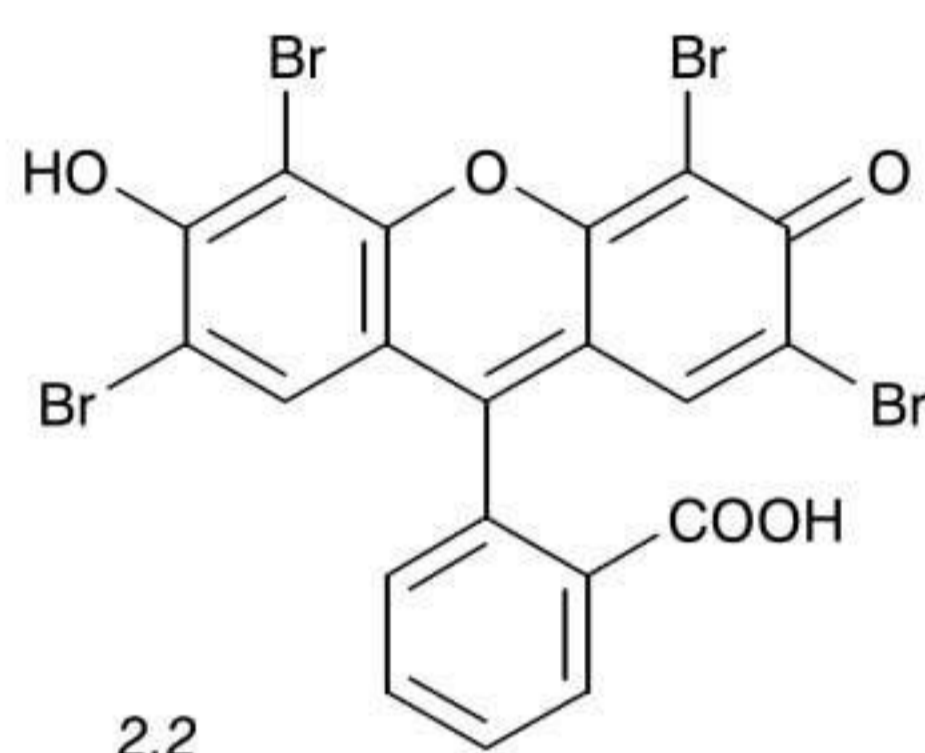
With the introduction of synthetic dyes, attempts were made to prepare pigments from them by methods based on those that had been used with the natural dyes. Many soluble azo dyes can be rendered insoluble by precipitating them as the salts of heavy metals in the presence of so-called alumina hydrate. This method will be treated in detail later and here only the making of pigments from acid dyes and basic dyes will be mentioned. The use of alumina hydrate as a basic substrate for making pigments from dyes is now, however, of diminishing commercial importance.

Alumina hydrate is made by slowly adding a 10% solution of sodium carbonate to a well-stirred 10% solution of aluminium sulphate, thus producing a white gelatinous precipitate of aluminium hydroxide. This is colloidal in nature and even prolonged washing does not remove all the sulphate ions adsorbed on it, but by careful control a consistent product with a high absorption power for precipitated dyes can be made. The precipitants used were antimony, barium and aluminium salts in the presence of rosin. In the USA alone, some 400 tons p.a. of methyl violet (CI Basic Violet 3) were precipitated by these methods for use on copying paper and in typewriter ribbons. The advent of computers with printers and word processing facilities has made such products obsolescent.

Other dyes that were extensively precipitated for use in printing inks were erioglaucine (2.1) and eosine (2.2) but their light fastness is too low to be acceptable nowadays. The process was called 'laking' and the products were termed 'lakes'.



Cl Acid Blue 9



Cl Acid Red 87

2.2.2 Dyes converted by precipitation with complex acids – 'toners'

In the early years of the 20th century efforts to improve the properties of pigments prepared from basic dyes took a fresh direction: precipitation of the pigments using the mordants that were employed when the same substances were being used as dyes. The light fastness of the resulting pigments remained poor, however.

Another approach was much more successful. It had been noted in biochemical work that some amines could be precipitated by treatment with acid in the presence of sodium phosphate and sodium tungstate or molybdate. When these precipitants were tried on basic dyes, pigments were produced with a higher light fastness than that of the parent dyes. This important discovery was patented by the Bayer company in Germany just before the First World War, but the shortage of tungsten and molybdenum resulting from the demand for these metals for use in armoured steel during the war delayed the exploitation of this discovery until peace returned.

Between the two world wars it was found that there was no need to isolate the complex acids used as precipitants; they could be used in solution. The use of mixed solutions of phosphotungstic and phosphomolybdic acids was also studied, as well as the effects of changing the pH of the solutions used and of various heat treatments after precipitation on the colour of the pigments produced.

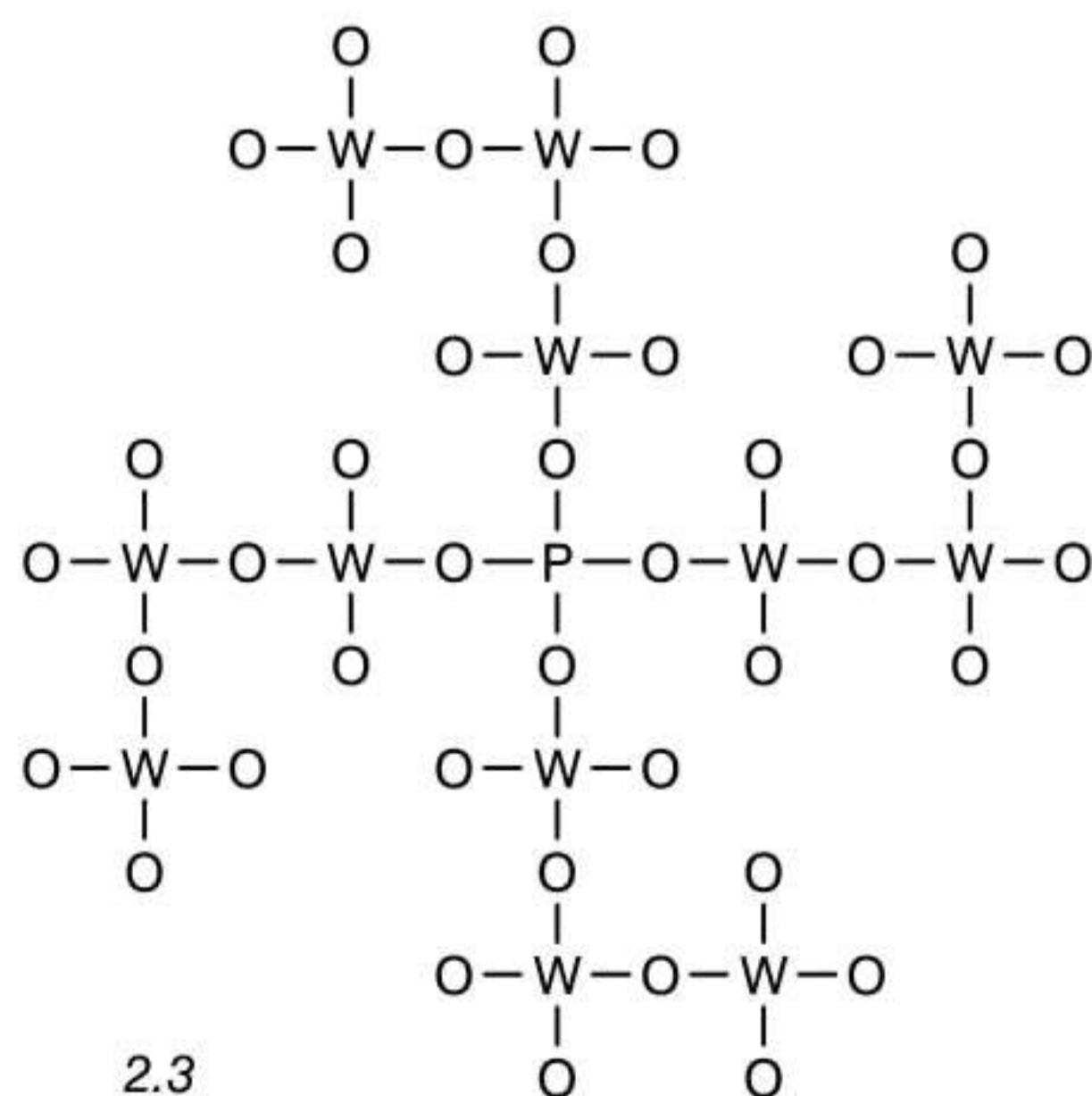
The Second World War again resulted in a shortage of tungsten and molybdenum and in an effort to overcome this the so-called 'copper toners' were made by precipitating basic dyes with copper(II) hexacyanoferrate. The resulting products were less brilliant in colour

than their predecessors and lower in strength and light fastness. Despite being cheaper, they found only limited use when supplies of tungsten and molybdenum resumed after the war had ended.

At that time, manufacturers typically produced ranges of about fifteen pigments of this chemical type, comprising blues, greens, yellows and reds. Some were made by precipitating mixtures of dyes; for example, blue pigments of increasingly greener hue could be prepared by adding minor but increasing amounts of a yellow dye to a blue dye. Commercially significant differences in technical properties, as well as price, could also be achieved by changing the ratio of tungsten to molybdenum in the complex acids.

The chemistry of these complex phosphotungstic (PTA), phosphomolybdic (PMA) and mixed (PTMA) acids was not fully understood until X-ray diffraction methods were used to determine their structures in the early 1950s. This work has shown that the structure of these compounds is built up from WO_6 octahedra. By sharing two oxygen atoms a W_2O_{10} unit (which does not exist independently) can be formed. In the phospho-12-tungstic acid the sharing process is continued so that there are four W_3O_9 (hypothetical) units clustered around the central PO_4 group in the form of a tetrahedron.

The overall structure of the anion is shown in formula 2.3. Since the phosphorus atom has five positive charges, the overall negative charge on the ion is three, i.e. $[\text{P}(\text{W}_3\text{O}_{10})_4]^{3-}$. The hydrated free acid is thus phospho-12-tungstic acid, i.e. $\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4] \cdot 14\text{H}_2\text{O}$. There are other complex phosphotungstic acids known with different phosphorus:tungsten ratios, but only the 1:12 series has found use in pigment making. Since tungsten and molybdenum are isomorphous in these compounds, the use of any ratio of these two metals is possible theoretically in preparing the complex acids. In practice, ratios of 85:15 or 60:40 seem to have been found satisfactory for most purposes. Molybdenum is less expensive than tungsten and thus it might seem advantageous to use lower ratios, but the pigments thus produced tend to darken on exposure to light, an undesirable property. The ratio of dye cations to complex anions in the pigments is 4:1. The only examples of pigments of this type currently made are CI Pigment Blue 1, Greens 1 and 2, Violets 1, 2 and 3, and Red 81.



Phospho-12-tungstic acid ion

2.2.3 Vat dyes converted into pigments

Although vat dyes may be regarded as pigments in view of their water insolubility, they were first used as dyes. When prepared for dyeing, their particle size is an important technical factor that influences their rate of reduction (section 3.1.4). Particle size was found to be even more important when attempts were made to use vat dyes as pigments. Commercial success was only achieved when methods for further decreasing and controlling the particle size were found, so that bright and tinctorially strong pigments resulted.

The impetus for these developments came mainly from the need for pigments of high light fastness in car finishes, particularly when light-coloured cars became fashionable in the 1950s. The necessary white pigment (titanium dioxide) was available, but to make the desired off-white paints small amounts of coloured pigments had to be mixed with the titanium dioxide. In such formulations many pigments, particularly azo pigments, show much diminished light fastness, from ISO ratings of 7 to ratings of 3 or 4.

The light fastness of vat dyes is generally good, so they were tried out for this purpose. In the physical form available at the time the dullness and poor tinctorial strength shown by many vat colours was unacceptable. Work was put in hand to alter the purity, particle size distribution and in some instances the crystal modification to make them more suitable for pigmentary use. Vesce [7] of Harmon Colors and Gaertner [8] of Ciba-Geigy have given accounts of these developments.

The chemical classes of vat colours from which suitable pigments have been developed are anthraquinones, perinones, perylenes and thioindigos. Many vat dyes have been tested, but only about a dozen have met the stringent fastness standards demanded. Seven of those found suitable in all respects are shown in Table 2.1 and their chemical structures are given as 2.4 to 2.10.

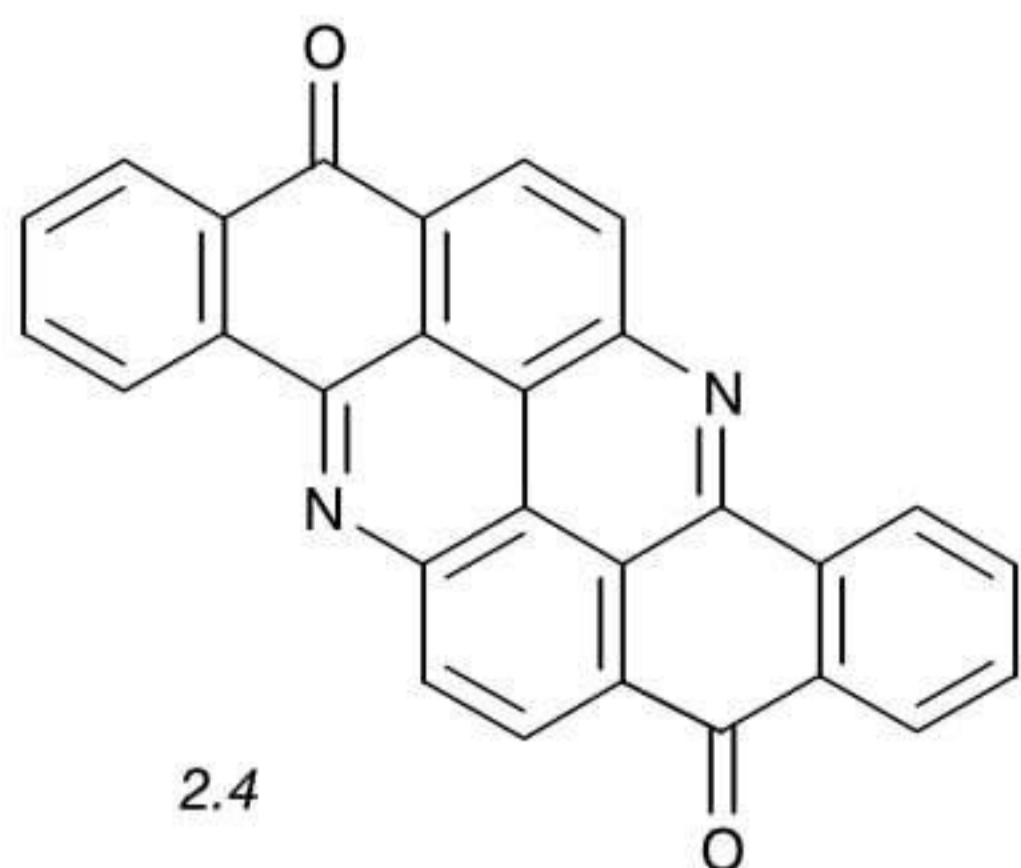
The methods used to convert these vat dyes into a suitable physical form (and in some cases, crystal structure) for use as pigments have been carefully guarded industrial secrets, revealed only in patents. The general principles are clear, however. One method is to reduce the vat dye in the usual manner to bring it into solution and then to re-precipitate it under very carefully controlled conditions. The other is to subject the dye to a fine grinding operation. Whichever approach is used, the aim is to reduce the mean particle size to below 1 μm (1000 nm).

Table 2.1 Typical pigments prepared from vat dyes

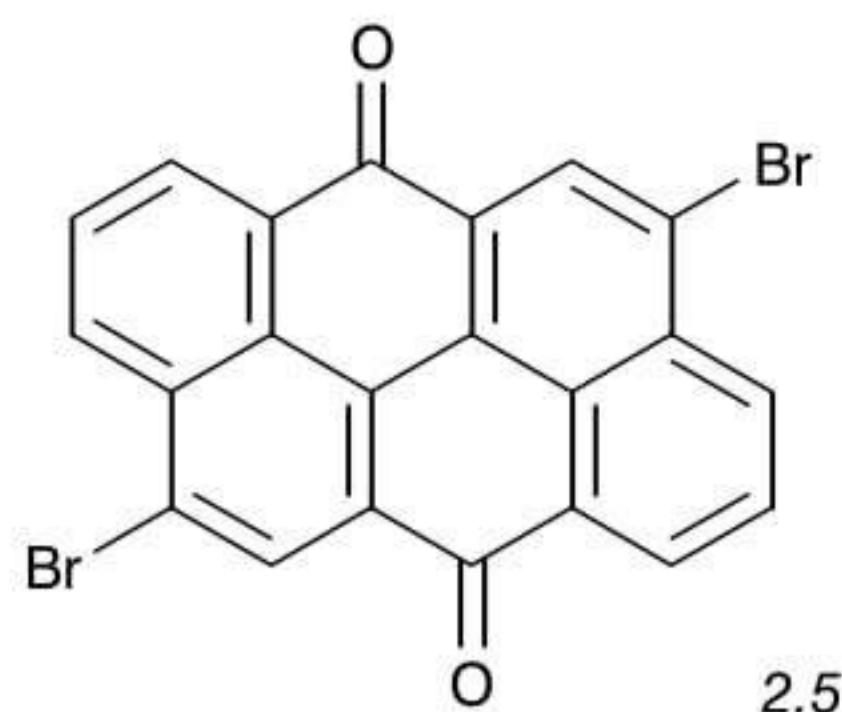
Structure No	Common name	CI Vat	CI Pigment
2.4	Flavanthrone Yellow	Yellow 1	Yellow 24
2.5	Anthanthrone Orange	Orange 3	Red 168
2.6	Anthrapyrimidine Yellow	Yellow 20	Yellow 108
2.7	Indanthrone Blue	Blue 4	Blue 60 ^a
2.8	Isoviolanthrone Violet	Violet 1	Violet 31
2.9	Perinone Orange	Orange 7	Orange 43 ^b
2.10	Perylene Maroon	Red 23	Red 179

a α -form only

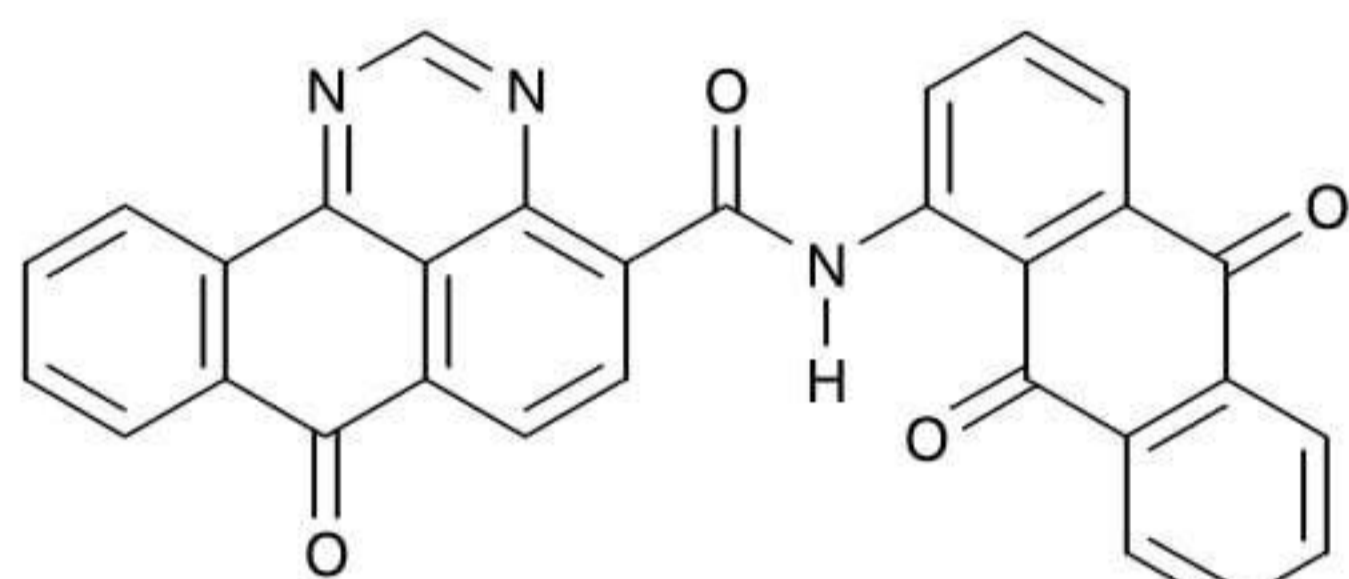
b *trans* form only



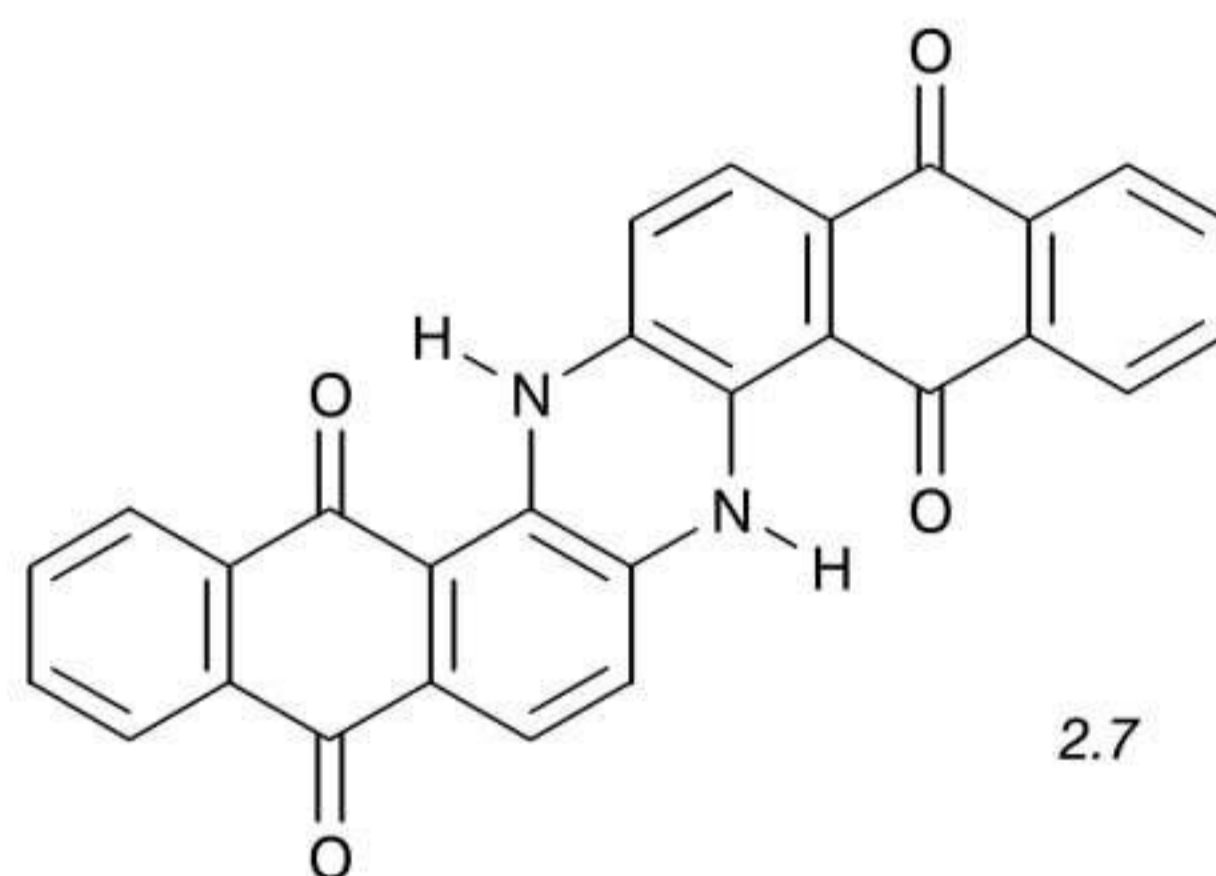
CI Pigment Yellow 24



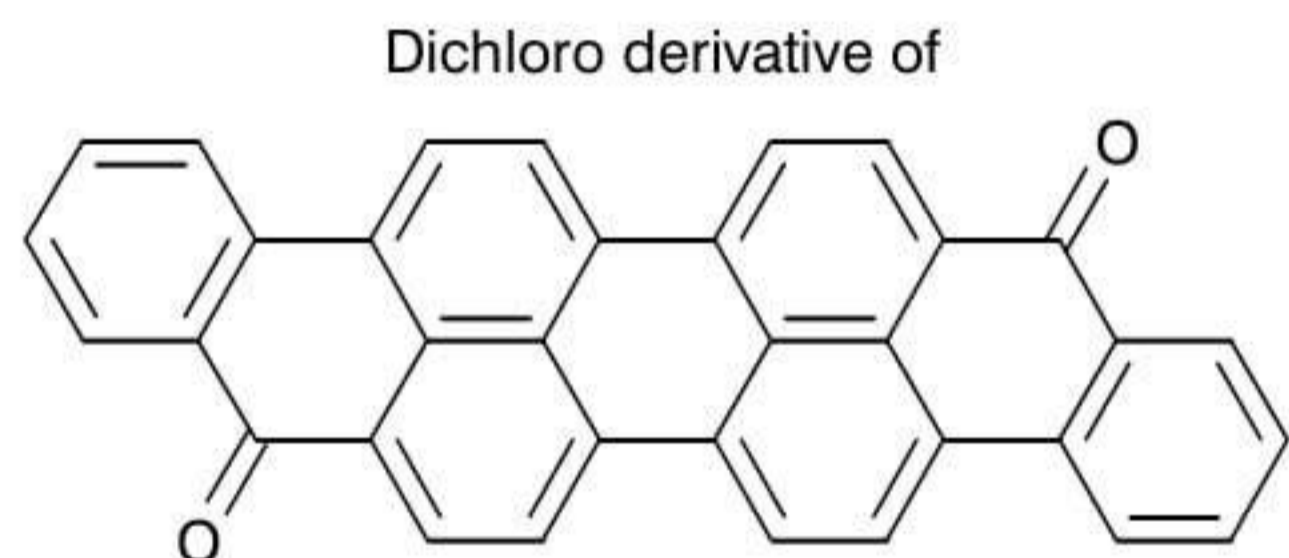
CI Pigment Red 168



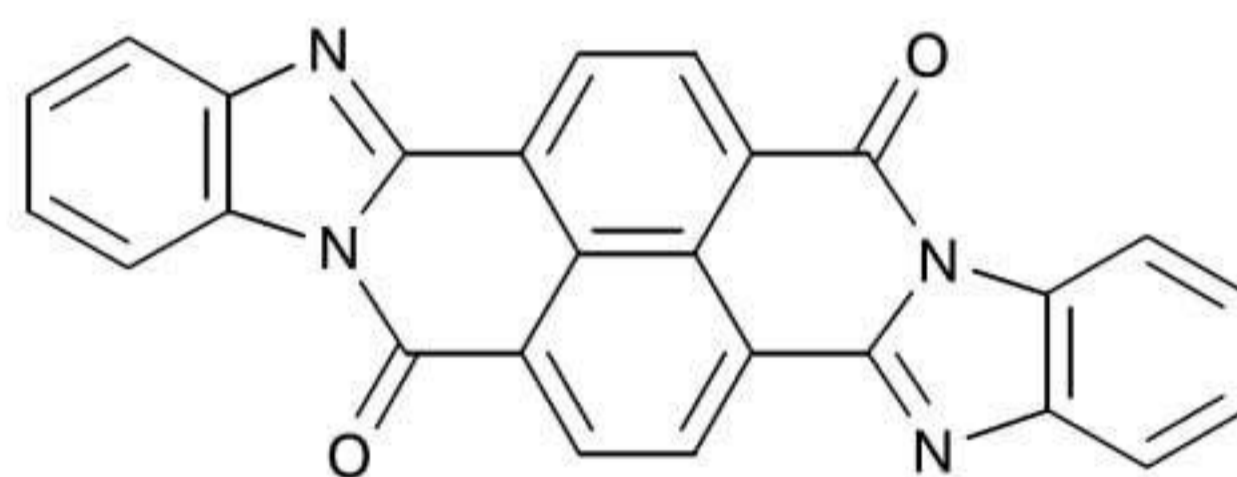
CI Pigment Yellow 108



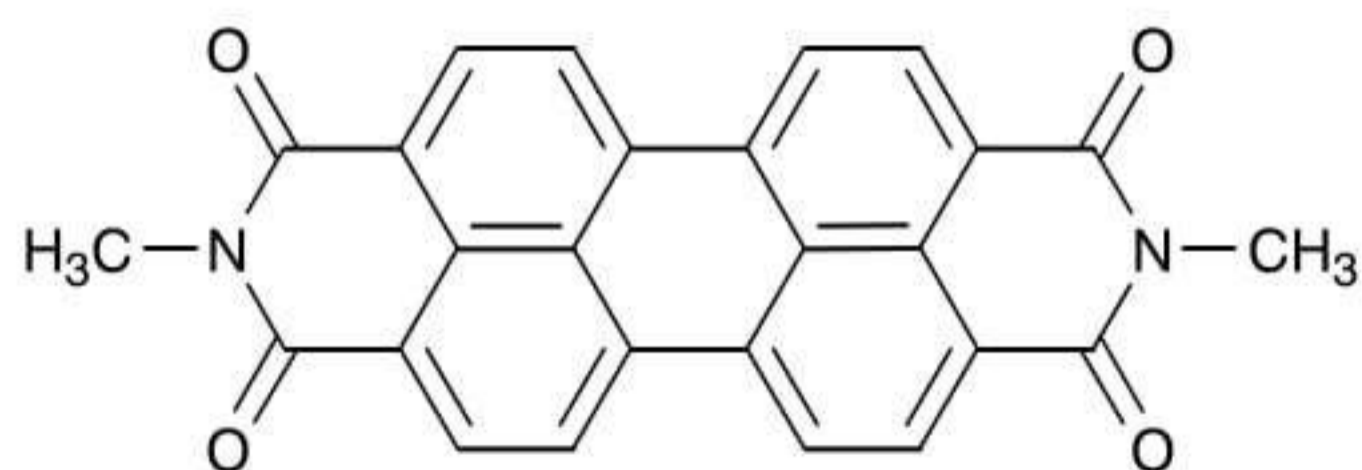
CI Pigment Blue 60



CI Pigment Violet 31



CI Pigment Orange 43



CI Pigment Red 179

Dry grinding can be carried out in two ways. The first comprises dry grinding in the presence of an inert substance such as salt, which can be removed by aqueous washing when the particle size of the dye has been sufficiently decreased. Alternatively, grinding in the presence of an organic solvent can be used. It is possible that local heating under the intense shearing conditions in the mill causes the dye particles to pass temporarily into solution. On

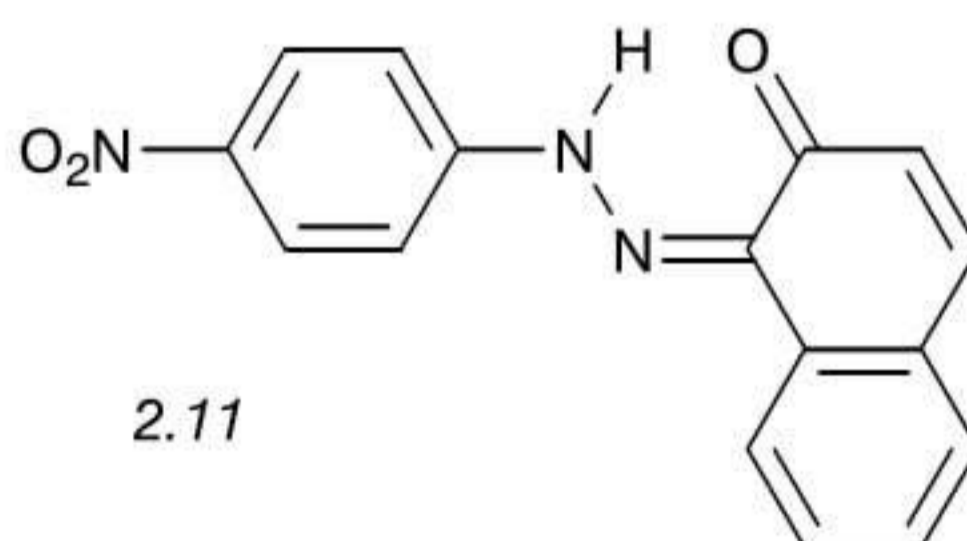
release from the local high-temperature zone the solubility limit is exceeded and the dye comes out of solution at a smaller particle size and in some cases with a different crystal structure. Sometimes hybrid processes of grinding in the presence of both salt and an organic solvent have been used. More detailed information has been published about the details of the dry grinding method in relation to phthalocyanine and quinacridone pigments, rather than vats, and this will be mentioned later.

The development of effective grinding processes for pigments, where the required mean particle size is much smaller than the wavelength of visible light (400–650 nm), was delayed because visible light microscopy could not be used. The desired size of the particles is below the resolving power of these instruments. The increased resolving power of ultraviolet microscopes was of some help, but still not sufficient for effective monitoring of the comminution processes. Centrifugal and surface area measurements were also useful, but laser light scattering, and in particular scanning electron microscopy, finally enabled the processes to be fully monitored. Although instruments for carrying out this research are expensive, together with X-ray diffraction they enabled both the size and shape of the particles and their crystal structure to be defined. The importance of pigment particles of submicron size is considered later (section 2.11).

2.3 AZO PIGMENTS

Azo pigments comprise by far the largest chemical class of compounds from which pigments are made, reflecting the wide range of aromatic amines that can be diazotised and the numerous compounds to which the resulting diazo compounds can be coupled, not all of course yielding pigments. The hues of the azo pigments range from red, yellow and orange to blue, in descending order of numbers of each hue.

The diazotisation and coupling reactions were exploited by the firm of Read Holliday in 1880 with the discovery of Vacanceine red, the first of the 'ice colours'. Cotton pretreated with 2-naphthol was immersed in a solution of diazotised 2-naphthylamine, prepared in the presence of crushed ice. Para red (2.11), however, patented by the same company in 1887, achieved much more success. This was applied to cotton in the same way using 2-naphthol and diazotised *p*-nitroaniline. Para red was also manufactured and marketed as a useful azo pigment.



2.11

CI Pigment Red 1 *Para Red*

Since the chemistry of the reactions involved in making both azo dyes and azo pigments is the same, discussion of these details is confined to Chapter 4. Only the structures of azo pigments and the special features of their preparation, largely concerned with preparing the pigments in their optimum physical form appropriate to their end use, are considered here. To do this, a classification of azo pigments is needed, as shown in Figure 2.1.

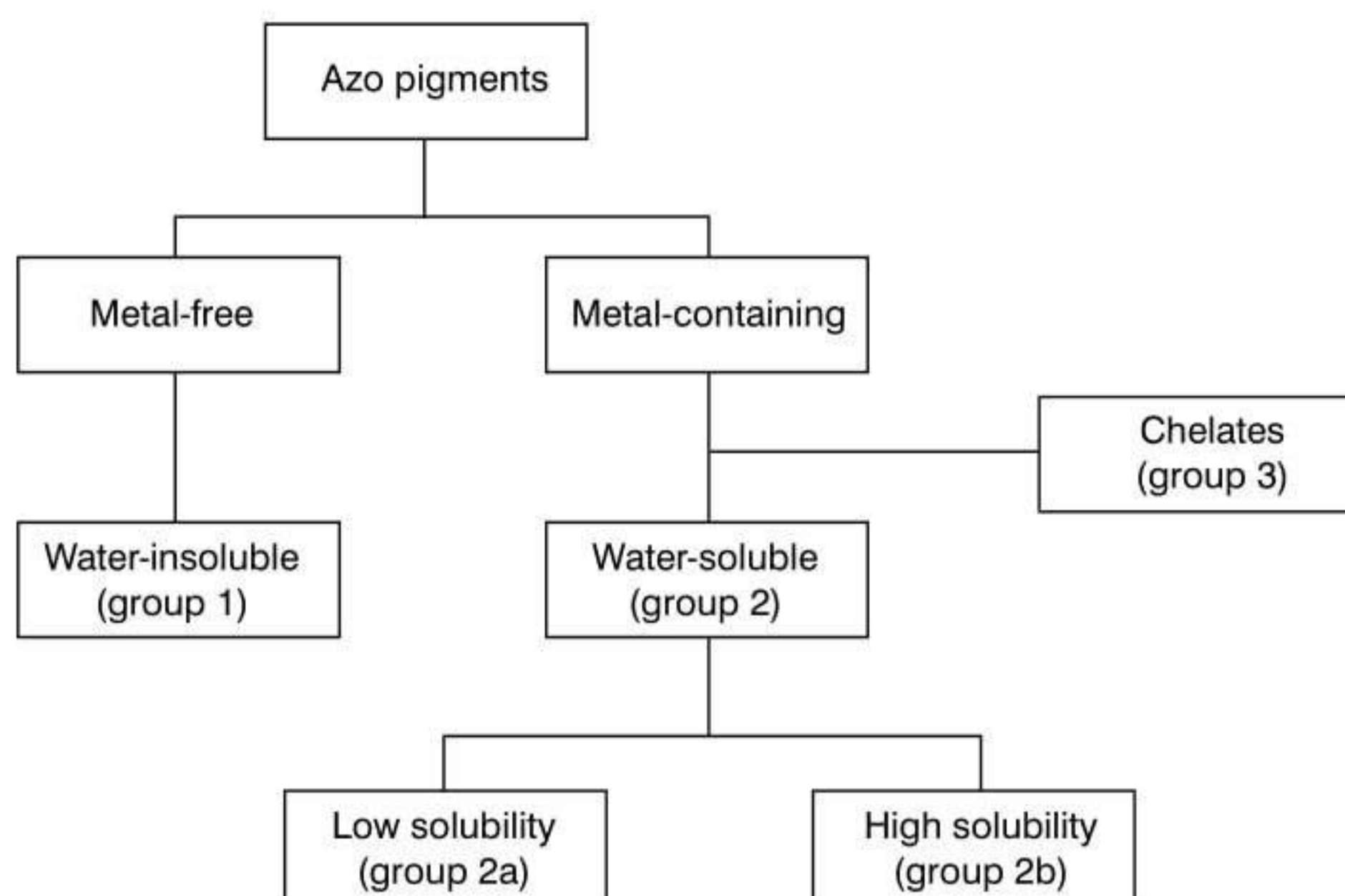


Figure 2.1 Classification of azo pigments

The primary division separates azo pigments into those that are metal-free and those that contain a metal atom in their structure. This means that those in the former group are entirely covalent in nature while those in the latter are not. An entirely covalent molecule possesses one property that is highly desirable in a pigment: insolubility in water. At the same time, such molecules are to some extent soluble in the organic media and solvents in which these pigments are generally used – paints, printing inks and plastics. The result is that unmetallised azo pigments have a tendency to diffuse in these media, giving rise to colour changes and poor fastness properties.

The need to make azo pigments that are metal-containing arises from the requirement to reduce the aqueous solubility of some azo colorants to a sufficiently low level to make them usable as pigments. The problem arises when either the amine or the coupling component (or both) from which the colorant is prepared contain substituents such as hydroxy or acidic groups. Depending on their number and location in the molecule, these can confer some degree of aqueous solubility on the resulting azo compound. The means adopted to reduce this solubility to an acceptable level depends on its degree, causing the pigment to fall into either group 2a or group 2b of the classification shown in Figure 2.1. All the pigments in group 2b are made from azo dyes. Those in group 3, of which there are only very few, are metal chelates.

2.3.1 Metal-free azo pigments

Pigments in group 1 made from 2-naphthol

Para red (2.11), which has already been mentioned, was the earliest pigment of this type. Toluidine red (CI Pigment Red 3) was first made in 1905. To make it, the amine *m*-nitro-*p*-toluidine (called MNPT in the pigments industry) is diazotised and coupled to 2-naphthol, the same coupling component that was used to make Para red.

There is probably more published information about the making of CI Pigment Red 3 than any other pigment, since in BIOS report 1661 [9] no less than six detailed works

processes are described. While all these processes yielded pigments with the same chemical structure, the hue and other properties of the resulting products differed sufficiently for them to be sold under different trade names.

Since one of the recurrent problems of the industrial production of azo pigments is to keep the coloration properties of the various batches constant within very close limits, it is useful to see the effects of changes in the process variables. They are set out in Table 2.2 [10]. In order to see which of these many variables had the greatest effect on the pigment properties, Hildreth and Patterson [11] investigated the effects of changing the following variables on the colour of the resulting pigments:

- (a) concentration of coupling component
- (b) pH of coupling
- (c) temperature of coupling
- (d) effect of the use of dispersing agent in the coupling bath.

The effects of the changes in the preparation methods were assessed by measuring the colour of the pigments in draw-downs and the particle size distributions of the powders. It was found that changes in all the listed variables could produce changes of several NBS

Table 2.2 Batch processes for preparation of Toluidine Red (CI Pigment Red 3)

	Helio Red RBL	Lithol Fast Scarlet GRN	Lithol Fast Scarlet RB	Lithol Fast Scarlet RN	Hansa Red B
<i>1. Diazotisation</i>					
m-nitro-p-toluidine suspn. (mol/l)	1	1.25	3.3	1.25	1.25
Temperature (°C)	2–5	0	0	0	0
Diazo conc. (mol/l)	0.59	0.71	1.1	0.71	0.71
Carbon addition	No	No	Yes	No	No
<i>2. Coupling component</i>					
Conc. of soln. of 2-naphthol in caustic soda (mol/l)	0.36	0.25	0.35	0.25	
2-naphthol, whether precipitated	Yes (HCl)	No	Yes (HCl)	No	Yes (HCl)
2-naphthol conc. at coupling (mol/l)	0.21 suspn.	0.061 soln.	0.245 suspn.	0.082 soln.	suspn.
pH at coupling	5–8	10	8	10	–
<i>3. Coupling conditions</i>					
Temperature (°C)	40	10	25	25	36
Method of adding diazo component	below surface	above surface	above surface	above surface	below surface
Time taken (hours)	2	2.5	1	2.5	3
<i>4. Subsequent treatment</i>					
Heating after coupling (°C)	50	none	90	95 (30 min)	70 (2.5 hr)
Washing	water (2 hr)	water	none	water	water
Drying temp (°C)	50–55	50–55	(paste made)	45	50–55

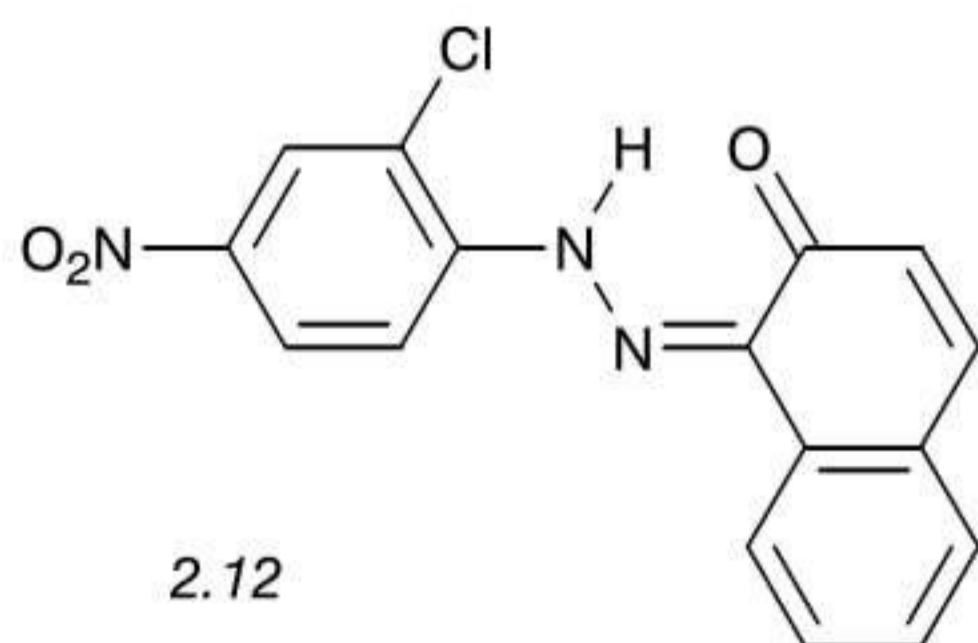
units of colour difference (one unit being about the commercial limit of acceptability between pigment batches). The tinctorially strong pigments were those with the largest proportion of particles below 500 nm in size and the largest surface area. The need for the strictest possible control of process variables to reduce batch-to-batch variability was clearly shown, but the variables needing the closest control were not the same for all the pigments investigated.

Both Para red and CI Pigment Red 3 are prepared using 2-naphthol as the coupling component. Other pigments made from the same coupling component, all discovered before 1910, are compounds 2.12 to 2.14 (Table 2.3). All these pigments, except CI Pigment Orange 5, are made by direct diazotisation of the appropriate amine using sodium nitrite and hydrochloric acid at temperatures around 0 °C, then adding the diazotised amine (the 'diazo') to an alkaline solution of the coupling component. There may be problems in carrying out diazotisation because of the hydrophobic nature of many aromatic amines. Two methods of overcoming this are frequently used. Either the hydrochloride of the amine is first formed, by stirring it with concentrated hydrochloric acid, or the particle size of the amine is reduced by dissolving it in concentrated sulphuric acid and then re-precipitating. Both methods aim to increase the rate of diazotisation, which tends to be slow on account of the low temperature and the small surface area for chemical attack, particularly if the amine particles have aggregated because of unfavourable storage conditions or other reasons.

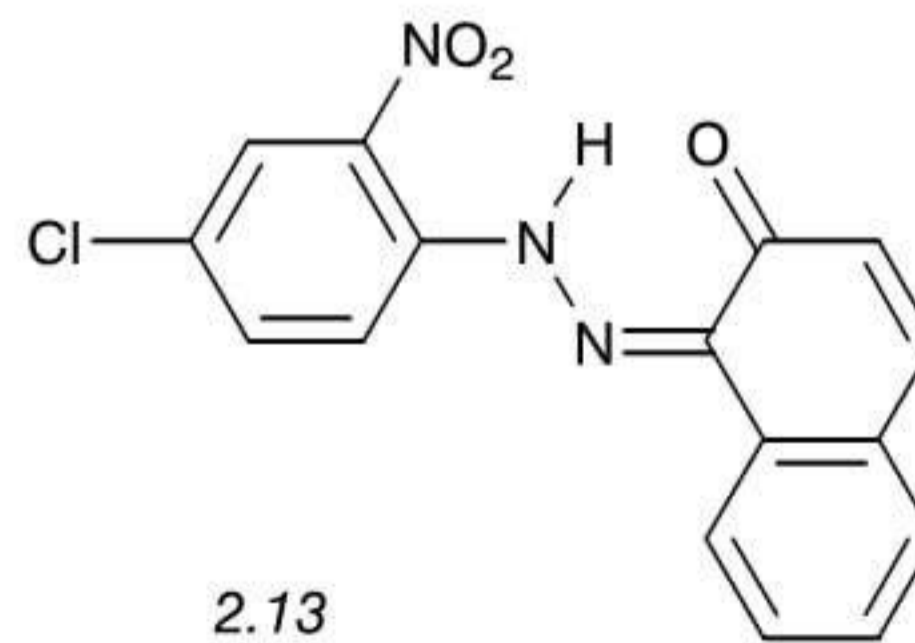
Another technical problem in diazotising these hydrophobic amines is how to decide when diazotisation is complete, especially when the diazo component is sparingly soluble

Table 2.3 Typical group 1 azo pigments made from 2-naphthol

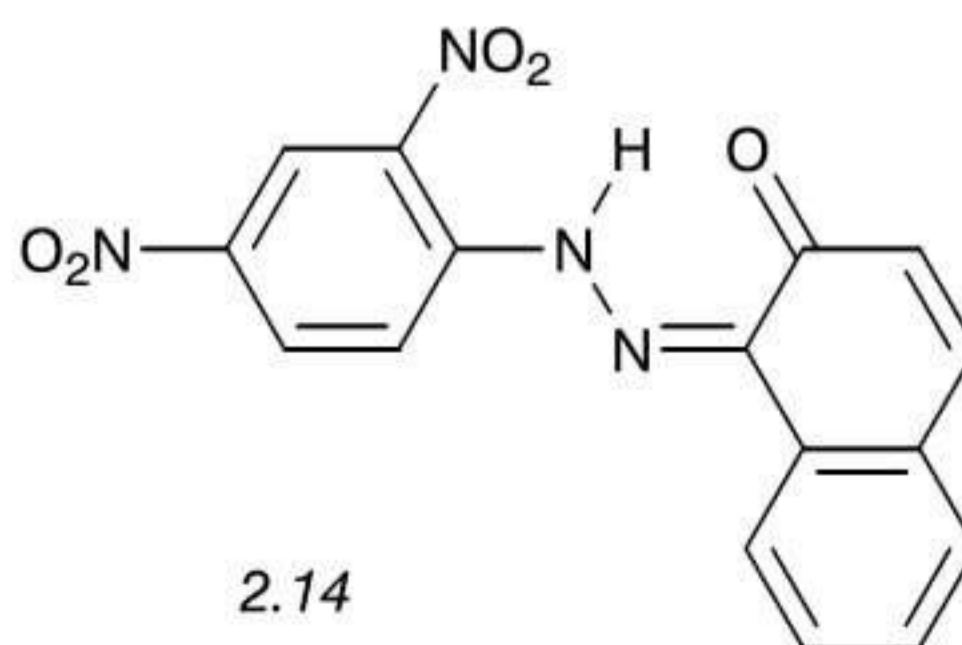
Structure No	Commercial Name	CI Pigment
2.12	Fire Red	Red 4
2.13	Red Toner	Red 6
2.14	Permatone Orange	Orange 5



CI Pigment Red 4



CI Pigment Red 6



CI Pigment Orange 5

and therefore appears in the form of a suspension. It is essential that the amine should be completely diazotised, because any unreacted amine will remain in the precipitated pigment with adverse effects on the colour and fastness properties. Diazotisation is complete if a test shows that free nitrous acid is present after sufficient reaction time has elapsed, as indicated by experience. A further test is carried out a few minutes later to confirm that a small excess still remains. The presence of nitrous acid produces an immediate and intense dark blue colour on starch-iodide paper when the diazo solution is spotted onto it. If this colour is not obtained the cause may be lack of acid or of nitrite. The amount of acid is increased if a test with pH paper shows insufficient to be present. Retesting with starch-iodide paper will then indicate whether more sodium nitrite is needed or not.

The amine that has to be diazotised to make CI Pigment Orange 5, namely 2,4-dinitroaniline, cannot be diazotised by the usual direct method. Nitrosylsulphuric acid ($\text{HSO}_4\cdot\text{NO}$) is needed and this is so corrosive that lead-lined vessels must be used for handling it. Even though this pigment has an unusually high light fastness in reduction (5–6 at 1/25 International Standard Depth, which is two units higher than most of the others in this group), the high costs of its production have led to a decline in its use.

Pigments in group 1 made from acetoacetanilides

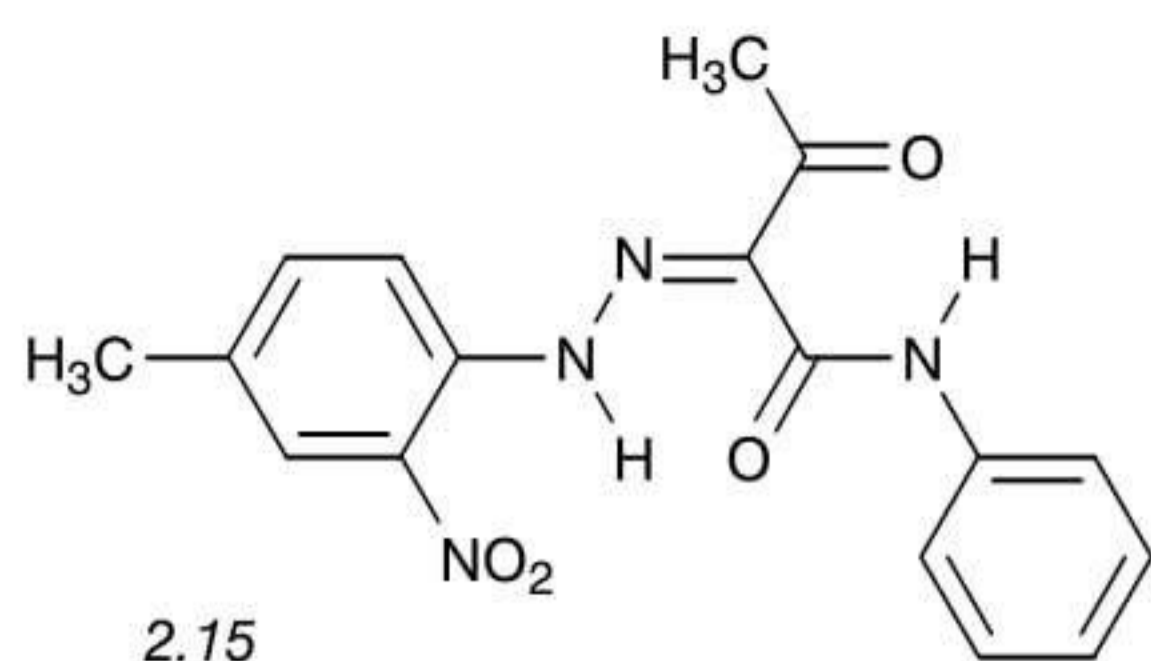
In the early 1900s several yellow pigments were made by coupling substituted nitroanilines to acetoacetanilides. They are commonly known as the Hansa Yellows (2.15–2.18); those that are greener in hue are identified by the increasing number before the 'G' in the suffix to their names (Table 2.4). The G (CI Pigment Yellow 1) and 10G (CI Pigment Yellow 3) pigments are the most widely used, the latter being much greener than the former but having only about one-third the tinctorial strength. The light fastness of all these pigments is 7 in full strength but falls to 4 in 1/25 International Standard Depth, with the exception of CI Pigment Yellow 3 which is rated 6+. This high light fastness in reductions makes CI Pigment Yellow 3, in the words of one of its many manufacturers: 'an inexpensive pigment with good to very good light fastness'. It is available in many physical forms and finds extensive use in paints and printing inks.

Disazo pigments made from substituted benzidines

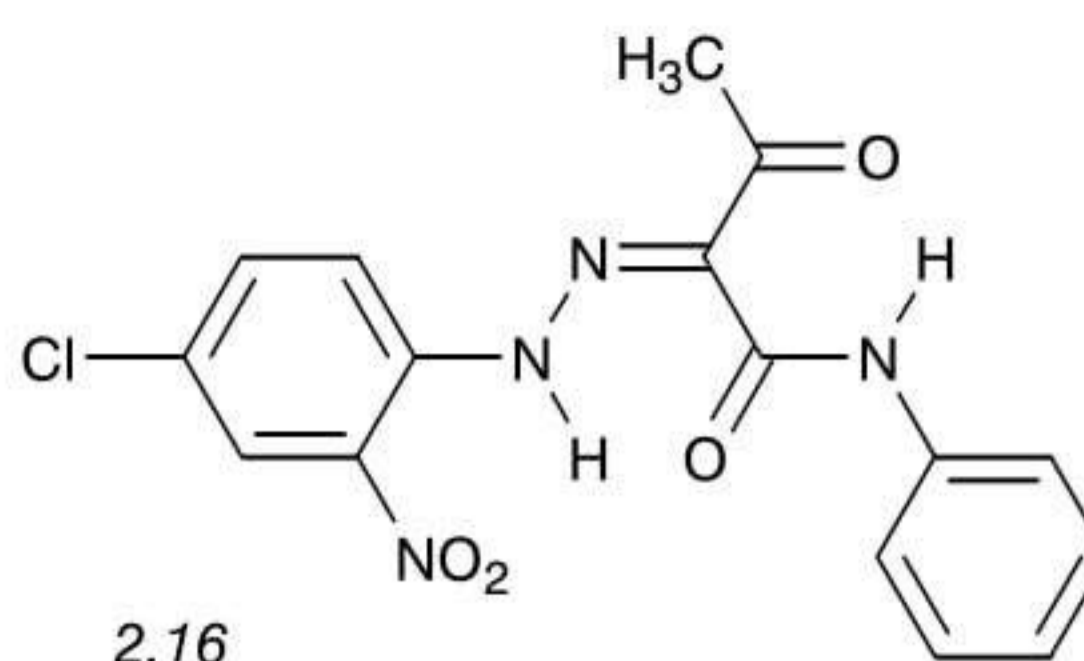
Benzidine is an aromatic diamine that can be tetrazotised and coupled to two molecules of a coupler such as acetoacetanilide. This gives a yellow disazo pigment that can be regarded as a double molecule of the monoazo pigments described above. The possibilities of making a

Table 2.4 Typical group 1 azo pigments made from acetoacetanilides

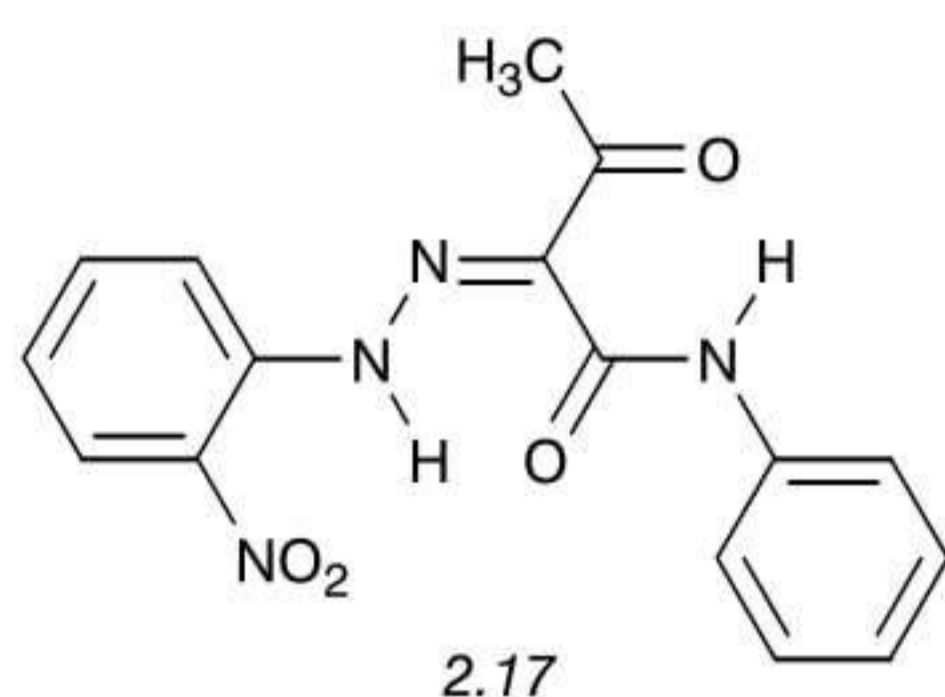
Structure No	Commercial Name	CI Pigment
2.15	Hansa Yellow G	Yellow 1
2.16	Hansa Yellow 3G	Yellow 6
2.17	Hansa Yellow 5G	Yellow 5
2.18	Hansa Yellow 10G	Yellow 3



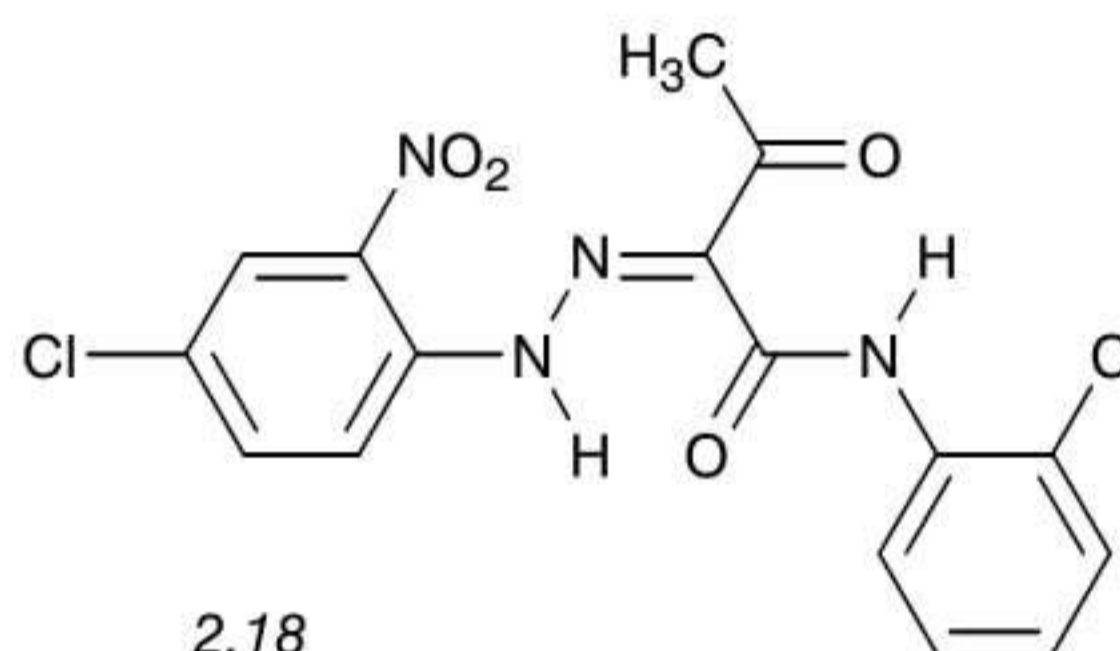
CI Pigment Yellow 1



CI Pigment Yellow 6



CI Pigment Yellow 5



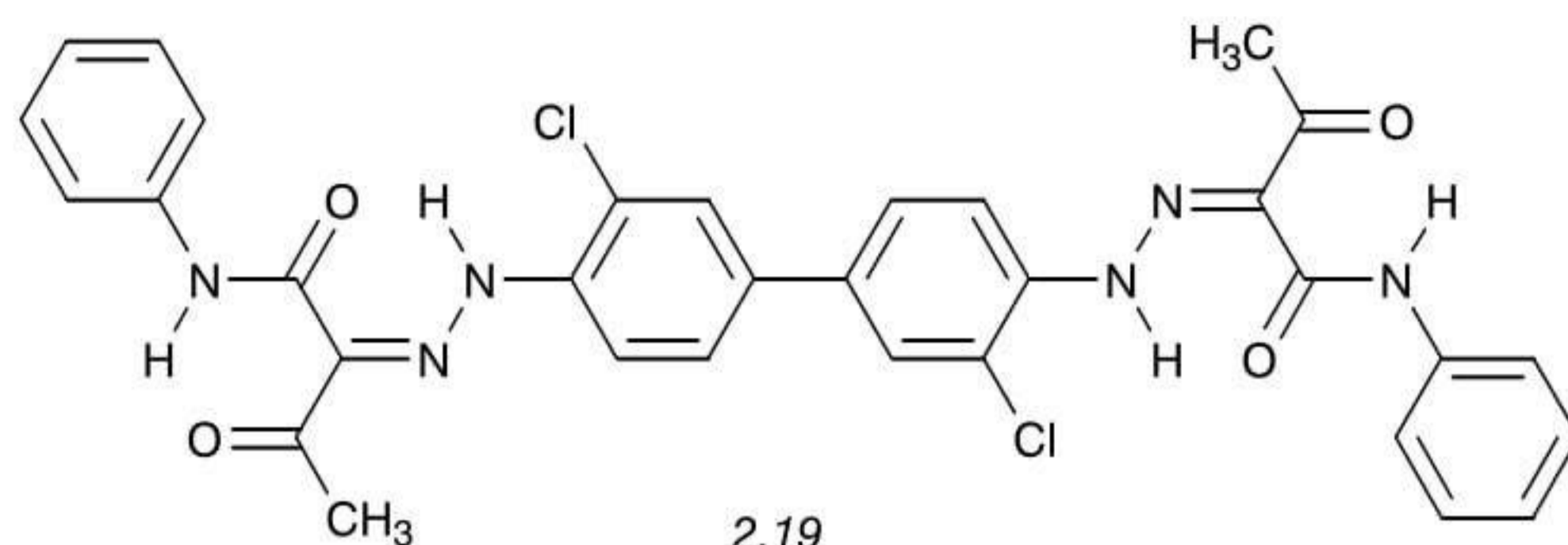
CI Pigment Yellow 3

range of colorants were well researched and both dyes and pigments of this general structure were produced. Of the commercial pigments, most were made from 3,3'-dichlorobenzidine or 3,3'-dimethoxybenzidine (*o*-dianisidine) but this is not the case with some of the disazo dyes.

The hues of these yellow disazo pigments are generally redder than those of the corresponding monoazo pigments made from the same coupling components, but their main advantage is that their tinctorial strength is three or four times greater. This is particularly useful in printing ink applications, where the flow properties of the inks depend on the loading of pigments in the formulations.

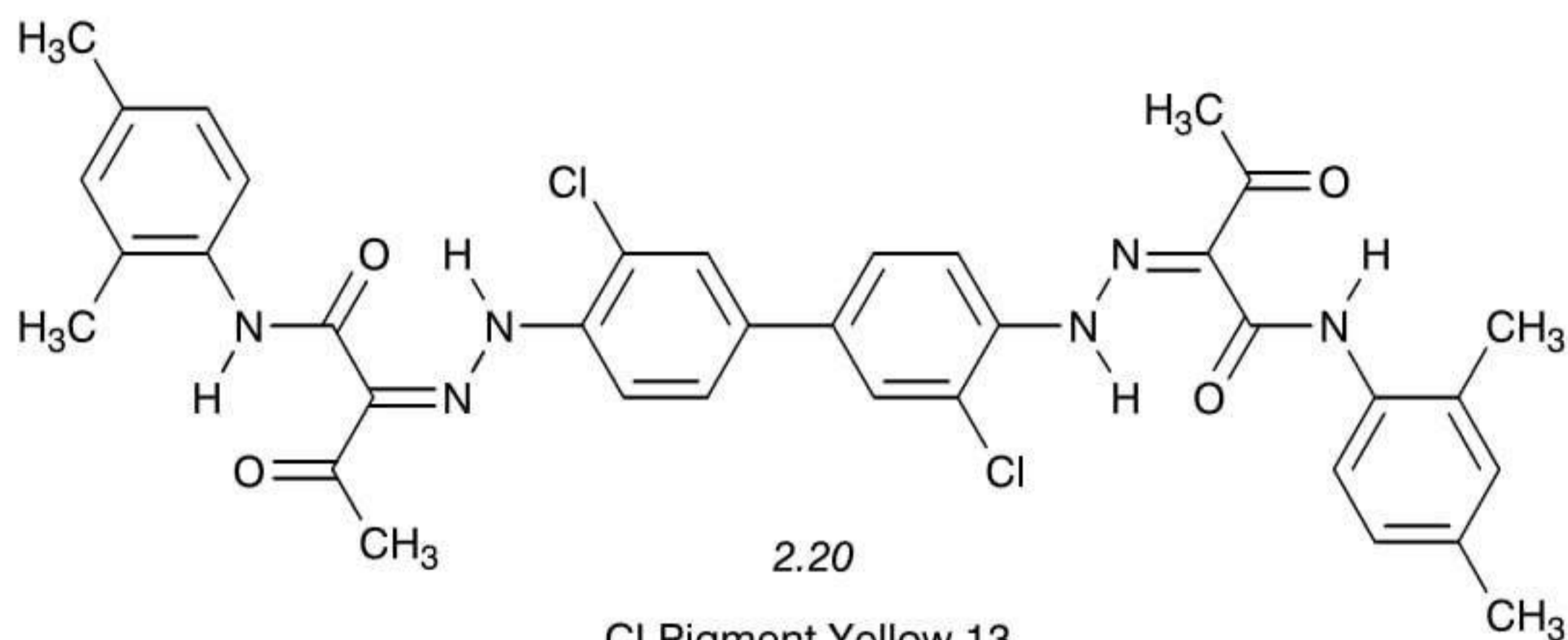
Disazo yellows have another advantage over monoazo yellows in that they show less blooming in plastics. Blooming is a tendency of pigment molecules to migrate to the surface of the plastic articles that they are used to colour. It can occur in moulding processes and also more slowly when in use. In either case it leads to colour loss and sometimes to contamination of articles coming into contact with the surface. The reason for the better performance of the disazo pigments is that their doubled molecular size leads to slower diffusion in plastics, but the matter is complicated by the presence of organic plasticisers and other additives in some types of plastics. On the other hand, the light fastness of the disazo yellow pigments is usually lower than that of the monoazo types.

The most widely used pigment of this type is CI Pigment Yellow 12 (2.19), made by direct tetrazotisation of 3,3'-dichlorobenzidine as the hydrochloride, followed by coupling of one mole of the product to two moles of acetoacetanilide. During the tetrazotisation reaction the green solution becomes yellowish brown. The analogous structure CI Pigment Yellow 13 (2.20) is made by tetrazotising 3,3'-dichlorobenzidine and coupling to acetoacet-*m*-xylylidide. It has found wide use in printing inks, including water-based formulations, and opaque and transparent types are available.



2.19

CI Pigment Yellow 12



2.20

CI Pigment Yellow 13

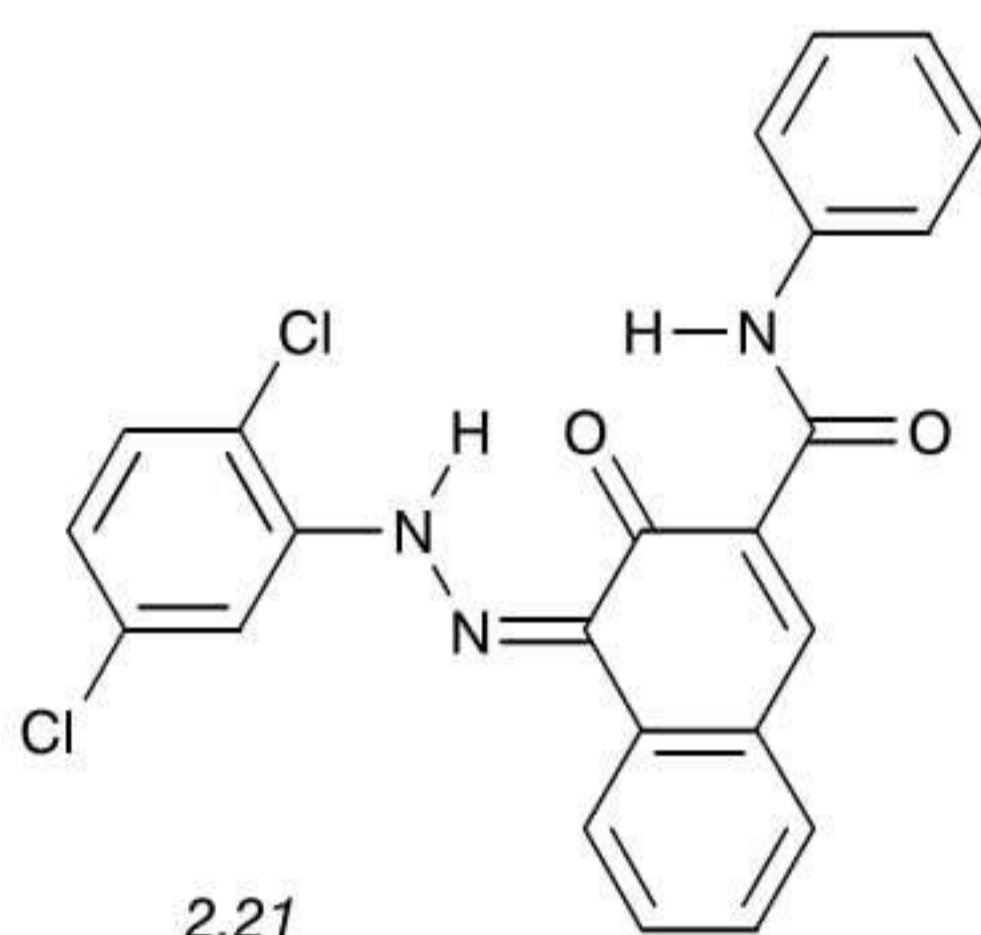
The influence of mixed coupling on the properties of CI Pigment Yellow 12 has been studied recently [12]. Carboxy- or sulpho- substituted derivatives of acetoacetanilide were evaluated as co-coupling components and analysis revealed that the state of the crystal and the particle size were changed and new diffraction peaks were observed. When these modified pigments were treated with a fatty amine such as stearylamine, the hydrocarbon chains enclosed the anionic groups in the co-coupler so that properties such as flowability, wettability and dispersibility in nonpolar solvents were greatly improved.

The undoubted technical merits of these pigments have been overshadowed, however, by the fact that they are simple derivatives of benzidine and therefore possibly carcinogenic. In 1971 the major European companies voluntarily ceased manufacture of dyes based on benzidine. Some of the subsequent results were unforeseen. As part of their consumer protection laws, the German government in 1994 framed some regulations in which the wording was not very precise, in particular on the point about whether the regulations apply to pigments as well as to dyes. There have been some amendments to clear up this point and a 1996 amendment excluded poorly soluble pigments with a relative molecular mass greater than 700. There is now a list (Table 4.1) of 22 different amines (including the diamine used for the preparation of CI Pigment Yellows 12 and 13). If a colorant, on reduction by a standard test method, can be shown as a possible source of any of these amines, then its use is prohibited. As with other apparently simple applications of scientific testing to legal matters (such as vehicle driving with a blood alcohol value above the legal limit) the sensitivity of the test method used and the test errors can give rise to problems. The whole matter is by no means finally settled, but remains important because Germany is both within the European Union and an important market for colorant producers throughout the world. The above restrictions on the usage of colorants yielding the banned amines apply equally to imported supplies.

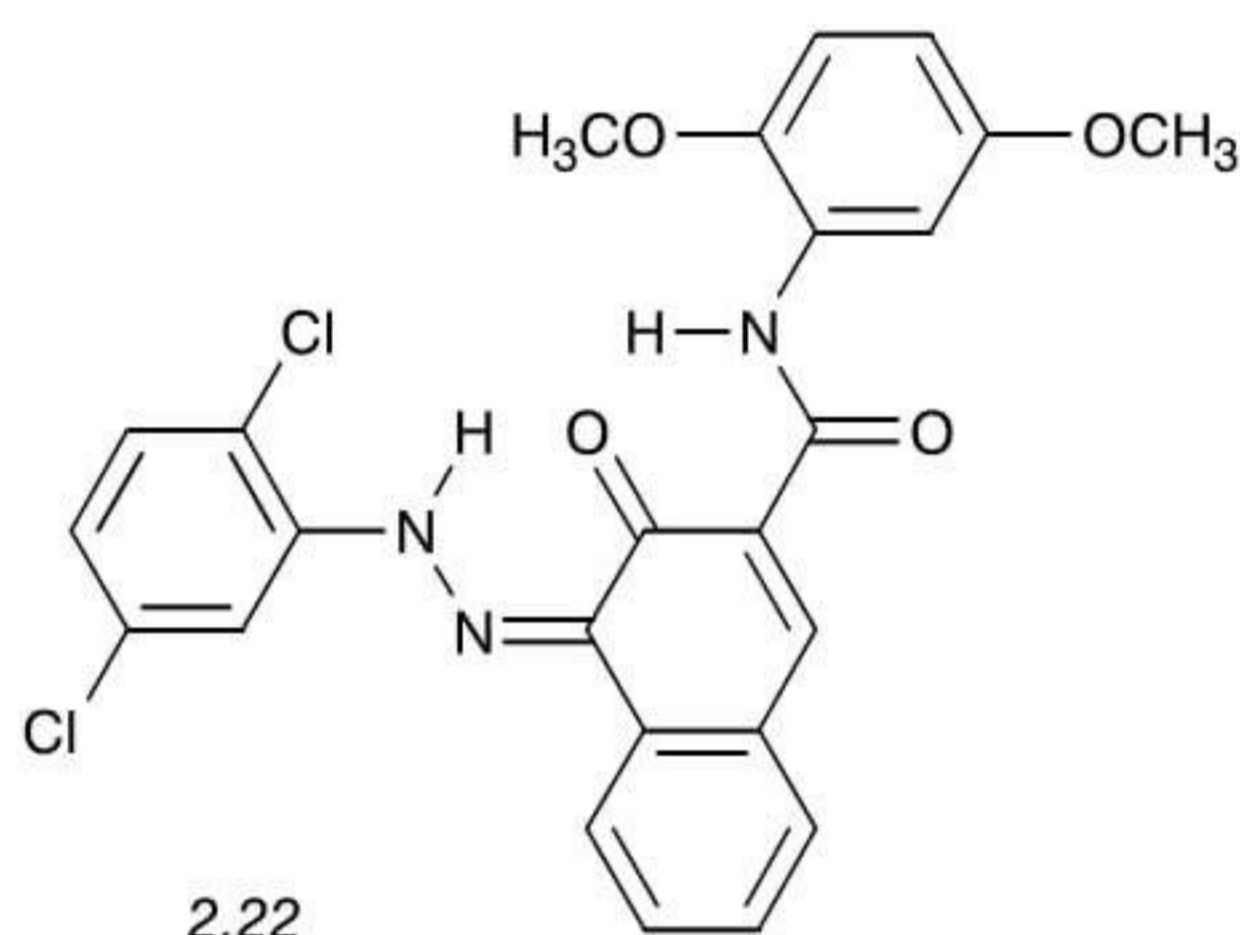
Pigments made from derivatives of 3-hydroxy-2-naphthoic acid (BON acid)

In about 1910, problems were encountered when pigments made using BON acid as the coupling component were reduced with alumina hydrate to make printing inks. The attractive bluish red of the pigments turned brown, according to Zitscher [13]. The difficulty was overcome by using anilides of BON acid instead of the acid itself. Several new pigments were introduced, the so-called Permanent Reds, only one of which, CI Pigment Red 2 (2.21), is currently made. The anilide of BON acid was marketed in 1912 as Naphtol AS (CI Azoic Coupling Component 2) for use in azoic dyeing and printing.

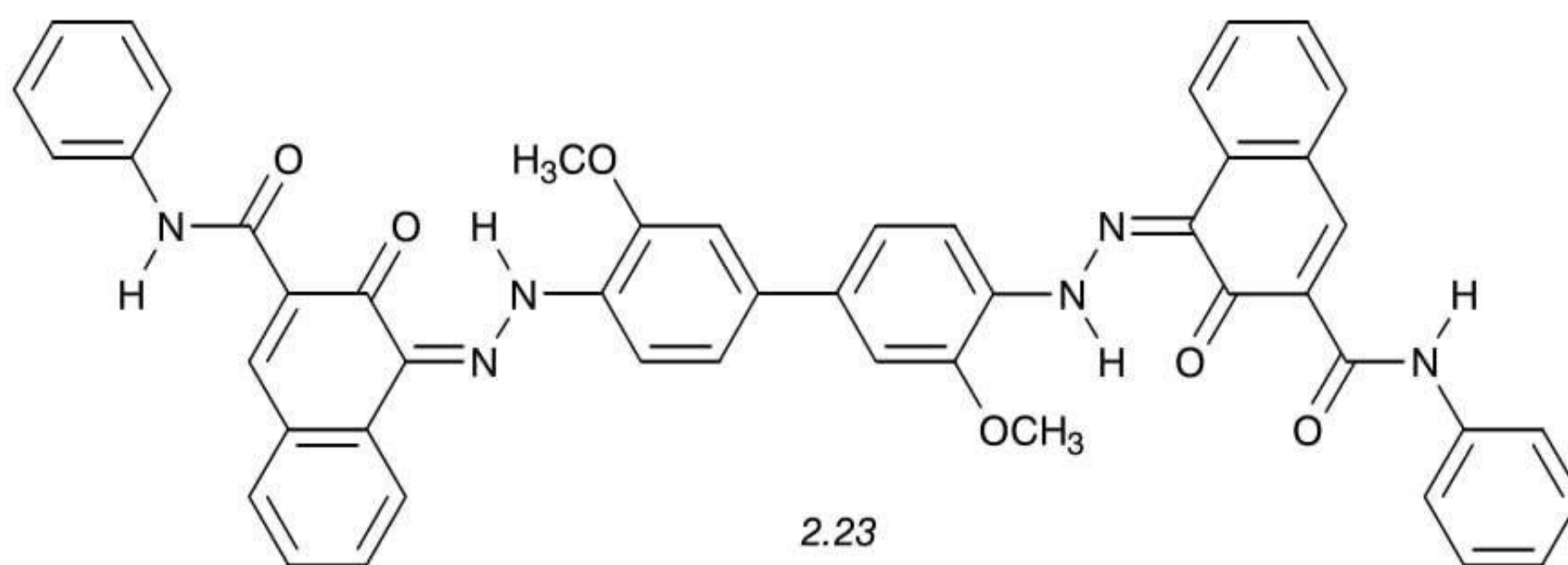
In the 1920s the hue range of pigments with this type of chemical structure was further extended by using other Naphtols as coupling components. These pigments have a light fastness of about 7 in full strength. Being rather complex hydrophobic structures they tend to have poor solvent fastness properties; this is a considerable disadvantage in the formulation of paints for vehicles, which are applied by spraying methods and are thinned with solvents. Two pigments discovered at this time and still in production are CI Pigment Brown 1 (2.22) and the blue disazo pigment CI Pigment Blue 25 (2.23), made by coupling tetrazotised *o*-dianisidine to Naphtol AS.



CI Pigment Red 2



CI Pigment Brown 1

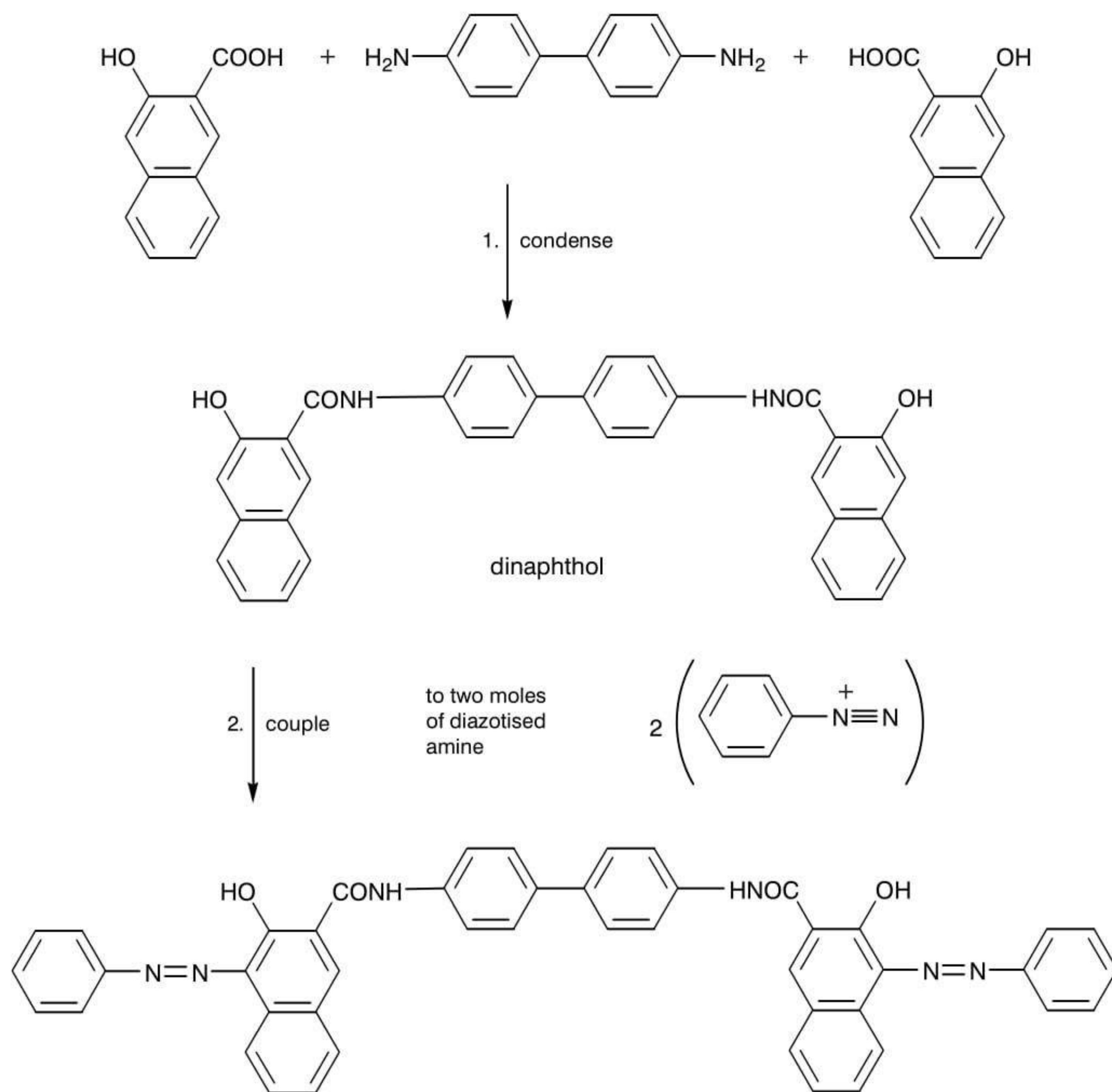


CI Pigment Blue 25

Azo condensation pigments

Although metal-free azo pigments have good chemical resistance their completely covalent nature leads to a tendency to bleed in organic solvents and to migration and blooming in

plastic formulations. It was found that the problems of migration and blooming decreased when the overall size of the molecule was increased. Attention turned to the possibility of doubling the size of the pigment molecules by first condensing one mole of benzidine with two moles of BON acid to form a dinaphthol and then coupling this to two moles of diazotised aromatic amine, as shown in scheme 2.1. Difficulties in the synthesis were soon encountered, because after one molecule of diazotised amine has coupled the solubility of the product in water is so low that it comes out of solution and does not couple with the second molecule of diazotised amine.



Scheme 2.1

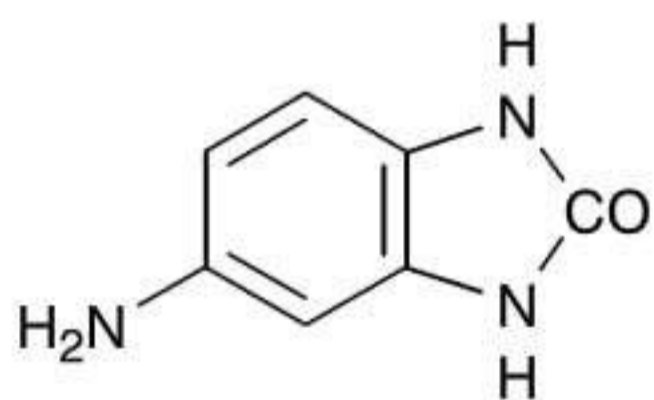
The solution to this difficulty, discovered by Schmid of Ciba in the early 1950s, is to reverse the order of the two steps. The diazotised amine is first coupled with BON acid and then two moles of this intermediate are condensed with one mole of benzidine in the form of its hydrochloride. The condensation is carried out in a high-boiling solvent such as nitrobenzene, when yields of 95% can be attained. These pigments have been called 'azo condensation pigments' in view of their method of synthesis.

Gaertner [8] has given some interesting insights into the problems of developing new products in a field of organic synthesis that has been the subject of well-funded and intensive research for nearly one hundred years. He stated that the Ciba company had used their new method to prepare well over 10 000 speculative samples. Those selected for development were given the commercial name of Cromophthals and initially eleven new pigments were marketed. Not all pigments now termed Cromophthals are of this chemical type, however, and allowing for this there are now about ten azo condensation pigments being sold. This illustrates the large expense involved in introducing new technical products and the difficulty of finding a place for them in a very competitive market, particularly as their initial selling price must be fixed at a level high enough to recoup their development costs. New pigments made from intermediates that are already in large-scale production seem to have the best chance of competing with existing products.

The small range of azo condensation pigments has become established only because they combine outstanding fastness to light, heat, solvents and chemicals, finding acceptance for use in paints, printing inks and the coloration of plastics and some synthetic fibres.

Benzimidazolone pigments

A further solution to the problem of reducing the reactivity of the carboxyl group in BON acid, when this compound is used as a coupling component in the preparation of azo pigments, was found in 1964 when the Hoechst company introduced their benzimidazolone pigments. A series of new Naphtol AS derivatives was made by condensing 5-aminobenzimidazolone (2.24) with BON acid. Other new coupling components have been made by condensing this compound with acetoacetanilides, which are used as coupling components for the Hansa Yellow pigments mentioned earlier.



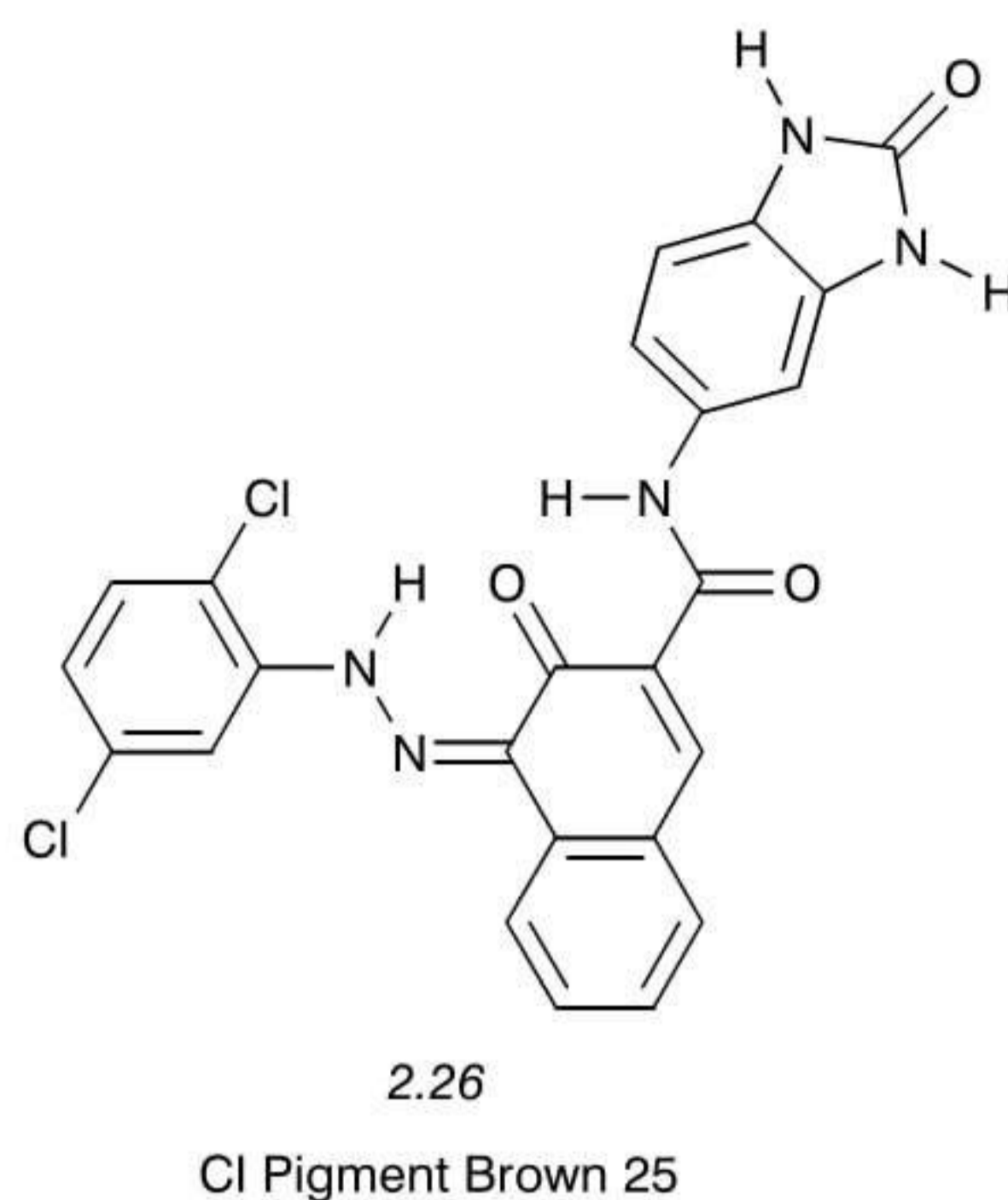
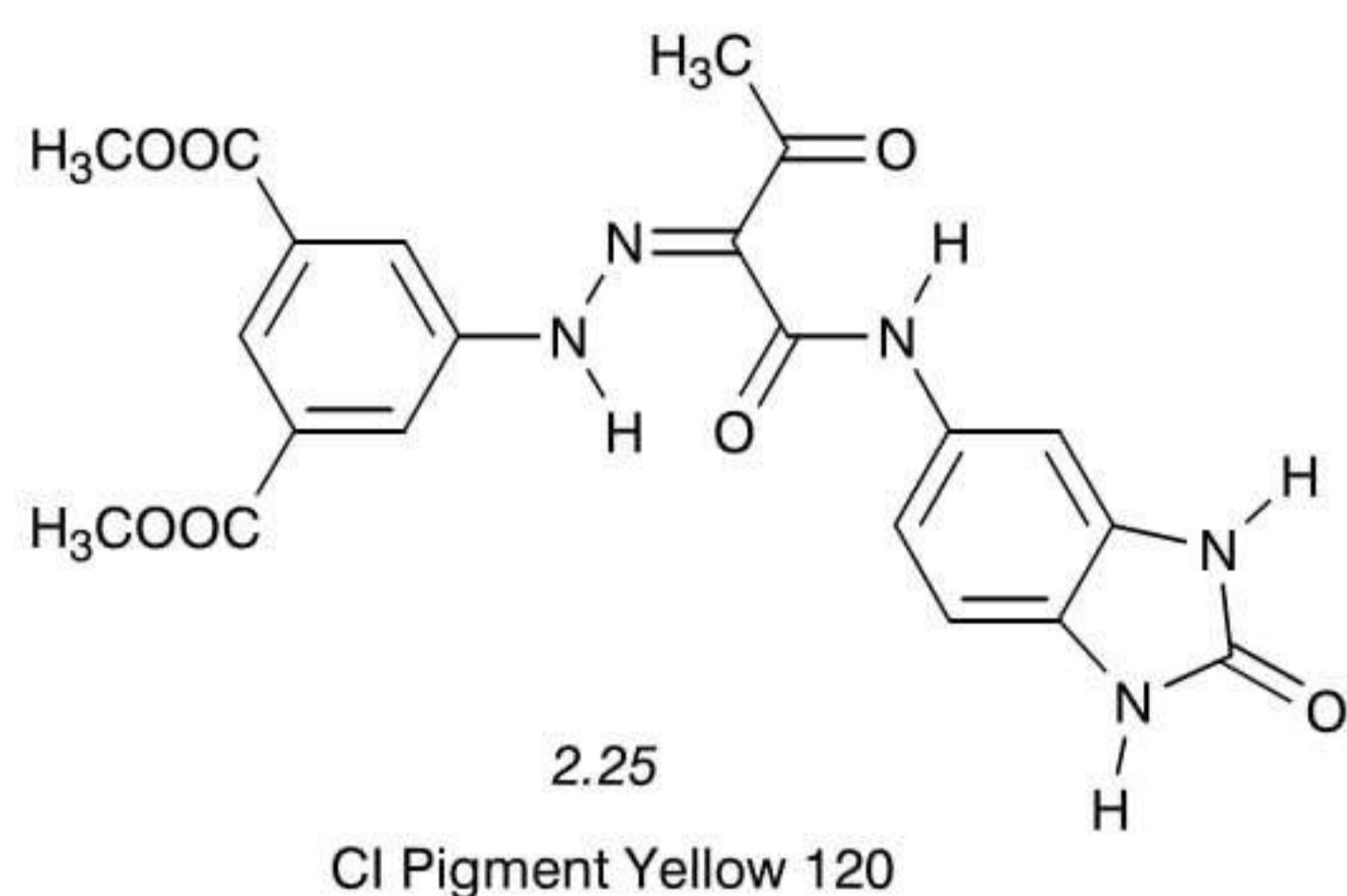
2.24

5-Aminobenzimidazolone

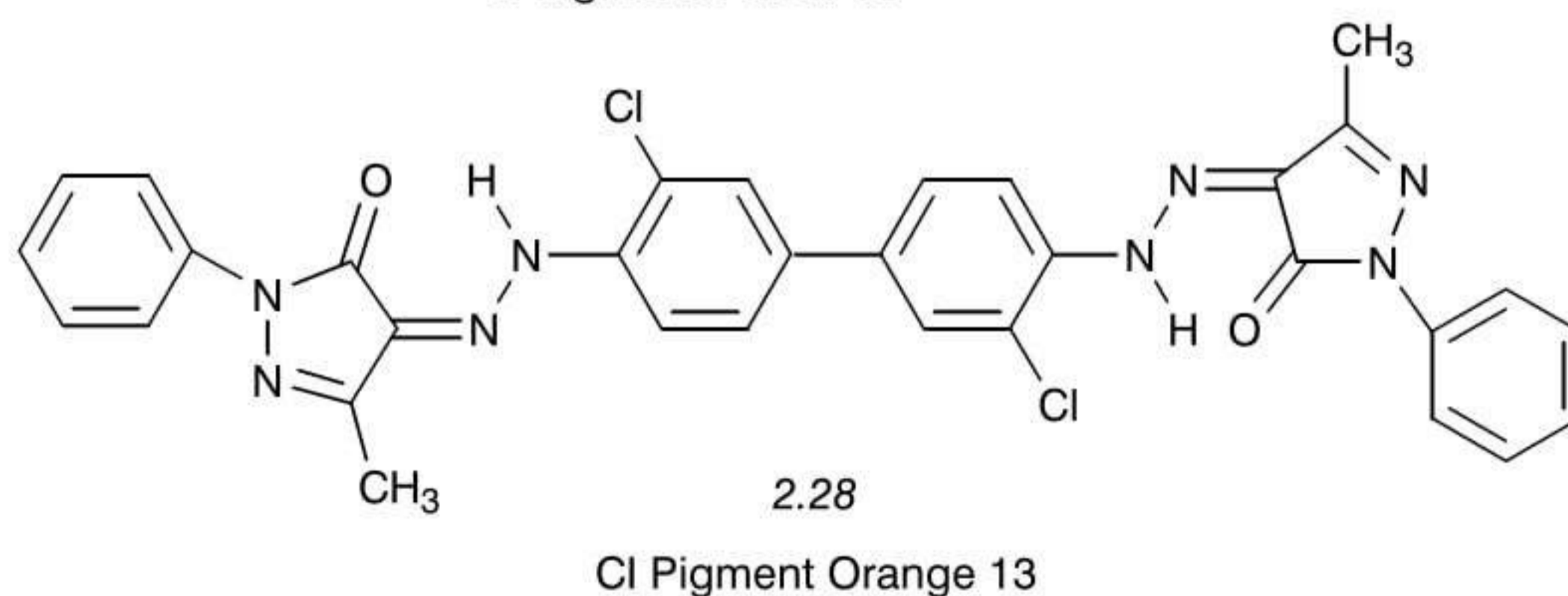
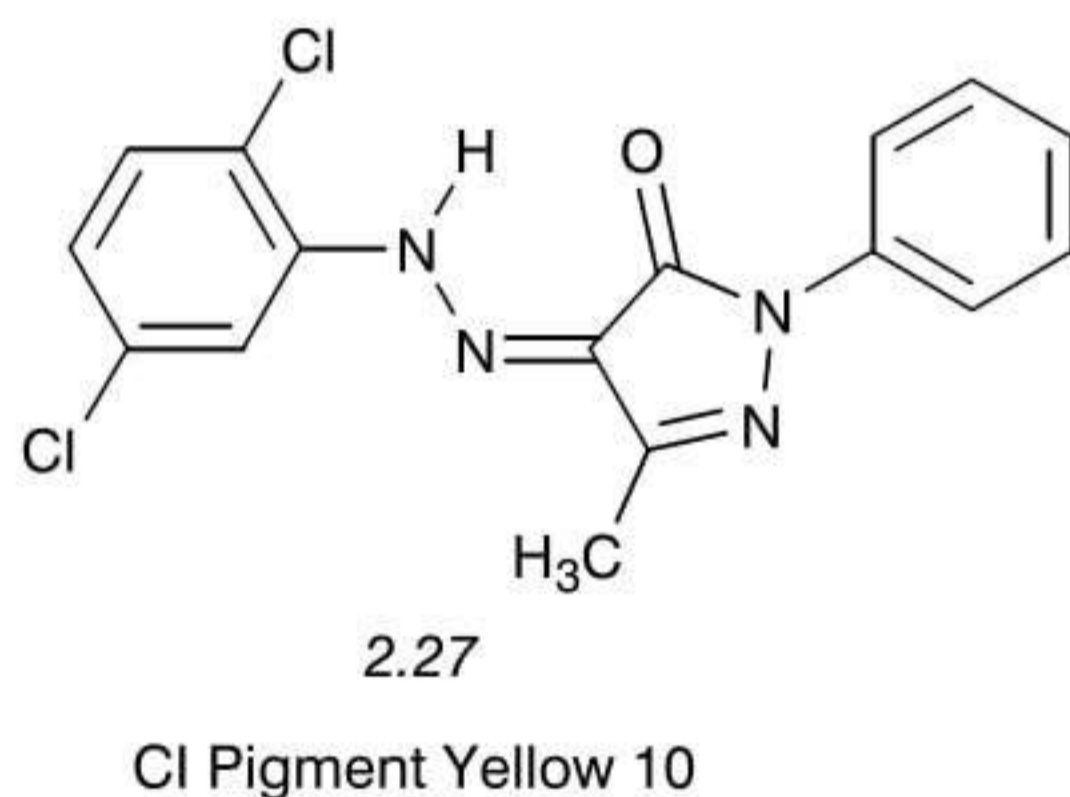
Two examples of benzimidazolone pigments are CI Pigment Yellow 120 (2.25) made by diazotising dimethyl 5-aminoisophthalate and coupling with *N*-(2-oxobenzimidazol-5-yl)acetoacetamide and CI Pigment Brown 25 (2.26) made from diazotised 2,5-dichloroaniline and 2-hydroxy-3-*N*-(2'-oxobenzimidazol-5'-yl)naphthalamide. Benzimidazolone pigments have given improved migration fastness and lower bleed in paint and PVC formulations, possibly because of hydrogen bonding between the carbonamide groups in adjacent molecules in the crystal lattice of such compounds.

Pigments made from pyrazolones

The last group of metal-free azo pigments are the pyrazolone compounds, the most commonly used examples being made from the coupling component 1-phenyl-3-methylpyrazol-5-one, also used in making azo dyes. The two most important pigments are



the reddish yellow monoazo Hansa Yellow R (2.27; CI Pigment Yellow 10), in which the amine diazotised is 2,5-dichloroaniline, and the disazo pigment CI Pigment Orange 13 (2.28), made from 3,3'-dichlorobenzidine. The latter pigment comes into the same category as the other disazo pigments mentioned earlier, as regards precautions in its use. In making both of these pigments the coupling component must be dissolved in concentrated caustic soda solution before diluting it prior to the coupling stage itself.



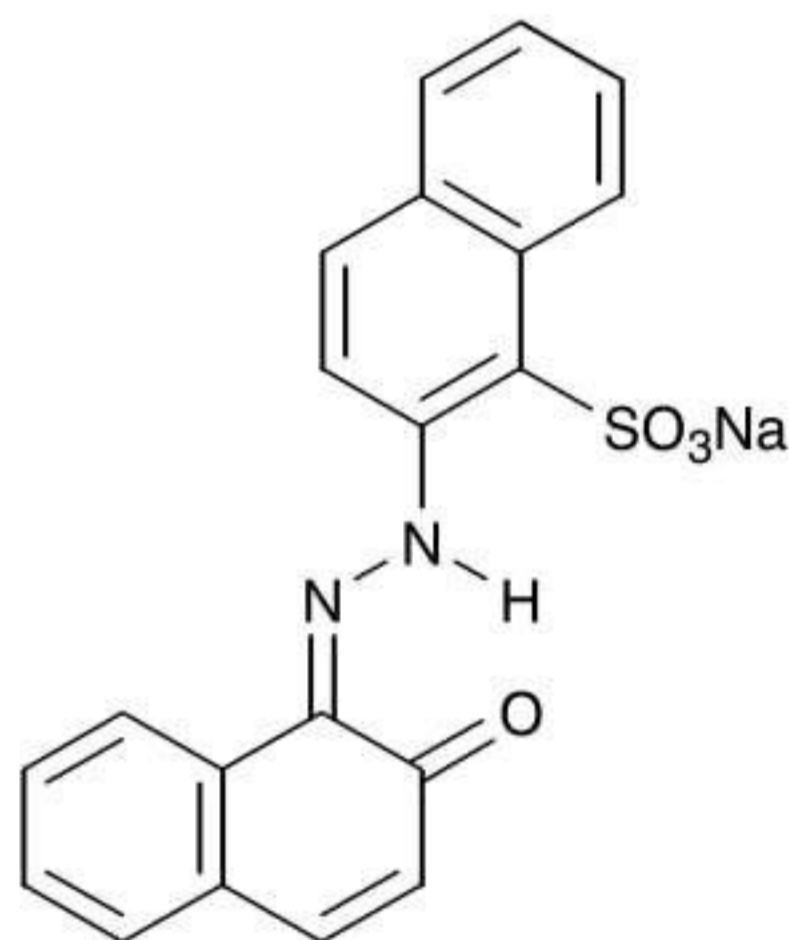
2.3.2 Metal-containing azo pigments

As already mentioned, certain azo colorants have low aqueous solubility but not sufficiently low for them to be usable as pigments. These azo colorants are prepared from amines and coupling components containing hydroxyl or carboxyl groups in their sodium salt form as a result of alkaline coupling conditions.

In many instances the aqueous solubility can be reduced to acceptably low levels by replacing sodium with a heavier metal, most commonly calcium, barium or manganese. These colorants fall into group 2a of the classification of azo pigments shown in Figure 2.1. When the solubility of the sodium-containing azo colorants is higher, so that they can be used and regarded as azo dyes, it may be possible to form heavy-metal salts only in the presence of basic substrates, usually alumina hydrate. These pigments consequently fall into group 2b of the classification. Whether a particular pigment falls into group 2a or 2b depends on the method used to make it in the form of these heavy-metal salts. The hues of the products formed using various heavy-metal precipitants are often so different that they are sold as separate commercial brands.

Pigments in group 2a

The first pigments in this group appeared about 1900 and were termed the Lithols. Lithol Red (2.29; CI Pigment Red 49) is made by diazotising Tobias acid (2-naphthylamine-1-sulphonic acid) and coupling it to 2-naphthol. Diazotised Tobias acid is zwitterionic and therefore sparingly soluble, forming a dispersion rather than a solution. This gives rise to difficulties in deciding when the diazotisation reaction is completed, which can be overcome by the method described in section 2.3.1. The product of coupling is the sodium salt, which is yellowish red with a solubility just low enough for it to be used as a pigment in printing inks. The pigment found wider use when converted to its barium and calcium salts, which are of a bluer hue.

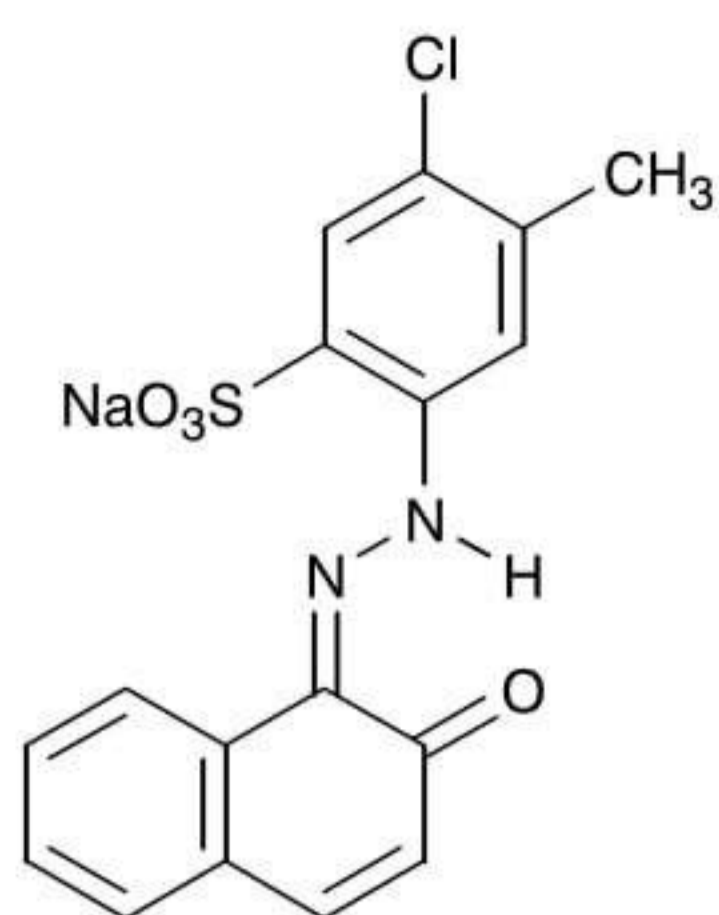


2.29

CI Pigment Red 49

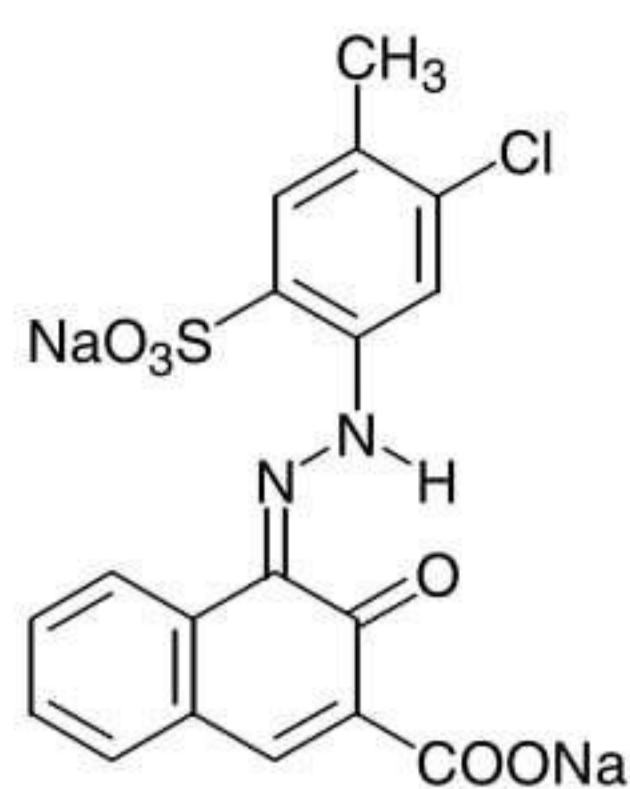
Lake Red C (2.30; CI Pigment Red 53), made by diazotising CLT acid (5-amino-2-chlorotoluene-4-sulphonic acid) and coupling to 2-naphthol, is a pigment that has also found considerable use in printing inks. The sodium salt gives prints with a strong bronze surface finish, which seems to depend on the presence of three moles of water of crystallisation to each mole of pigment. If these are driven off by strong heating the bronzing effect is lost and cannot be regained. The barium salt found wider pigment applications.

Tobias acid diazotised and then coupled to BON acid has been used as the manganese salt (CI Pigment Red 63) to give a bordeaux shade, but two other pigments (2.31; CI Pigment Red 48, and 2.32; CI Pigment Red 57) made from the same coupling component are of much greater current importance. The first is made from 2B acid (4-amino-2-



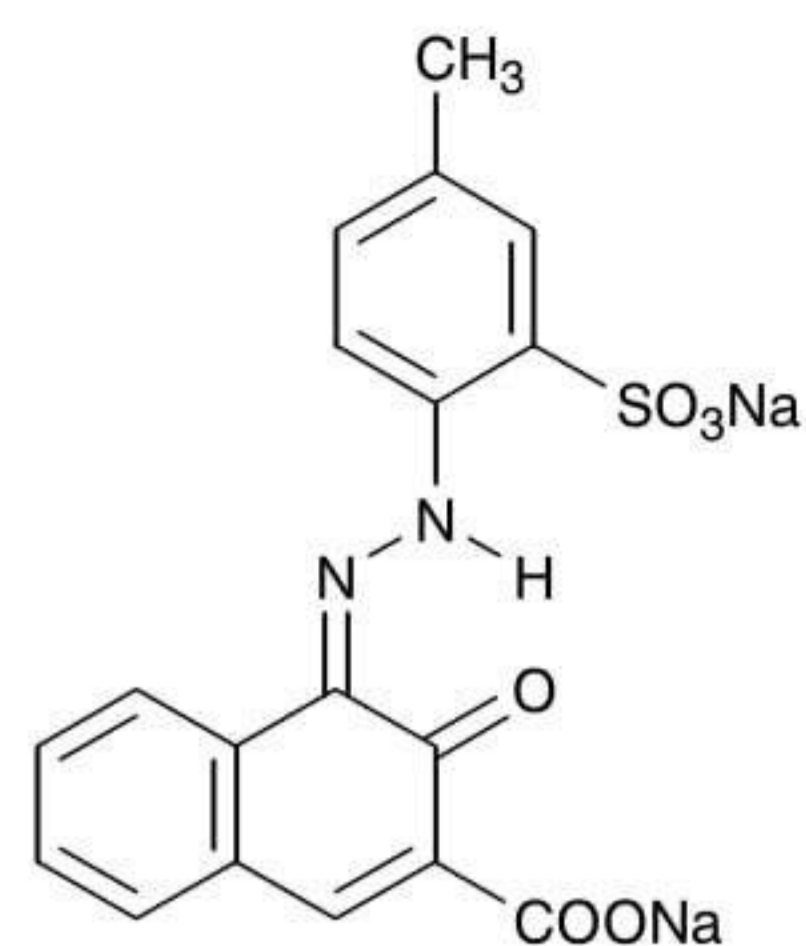
2.30

CI Pigment Red 53



2.31

CI Pigment Red 48



2.32

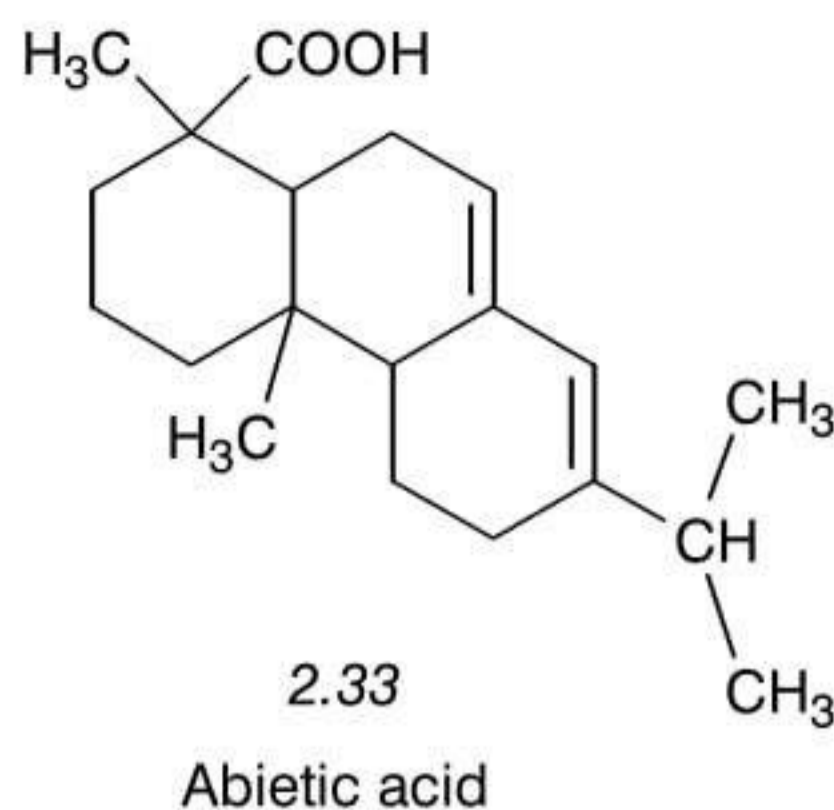
CI Pigment Red 57

chlorotoluene-5-sulphonic acid) and the second from 4B acid (4-aminotoluene-3-sulphonic acid). They are called 2B and 4B toners, as might be expected, whilst compound 2.32 is also named Lithol Rubine. The 2B toner is converted into strontium, barium, calcium and manganese salts, whilst the 4B toner is used as its calcium and barium salts. The principal use for both pigments was originally in printing inks, particularly in oil-based types. Nowadays, however, numerous specially prepared commercial brands are available with their physical properties adjusted for use in plastics, various types of paints and even, in the case of CI Pigment Red 57, as colours for cosmetics and pharmaceuticals. The specifications of these products, particularly as regards the absence of heavy metals, is exceptionally stringent. Specially designed plant, used only for pigment intended for these purposes, is needed.

Rosination

Long before such specialised uses of pigments in group 2a were considered, the process of rosination played an important part in their manufacture. In the preparation of all these pigments in the form of their heavy-metal salts, the method of metal exchange is to heat the sodium salt with a solution of the chloride of the required heavy metal. Outstanding technical advantages result if this metal exchange is carried out in the presence of rosin soap. The resulting pigments are more easily dispersed, of greater tinctorial strength and higher brilliance, imparting a glossier appearance to printing inks. Rosination is therefore a most important part of pigment technology.

Rosin is a natural product derived, along with turpentine, from the resin collected from certain American pine trees. It is graded by colour and the grade WW (water white) is used in the pigments industry. The acidic components originally contain about 40% L- and D-pimaric acid but during processing these are converted to abietic acid (2.33). Neoabietic, dehydroabietic and dihydroabietic acids are also present, according to Harris [14]. Rosin soap is made by dissolving the rosin in a hot solution of sodium hydroxide maintained at as low a temperature as possible consistent with keeping the soap in solution – it is almost insoluble in cold water. The hot solution, containing also the dissolved heavy metal chloride, is added to a dispersion of the sodium salt of the pigment. The whole is brought to the boil and, at a temperature between 80 and 90 °C, a marked colour change indicates that metal



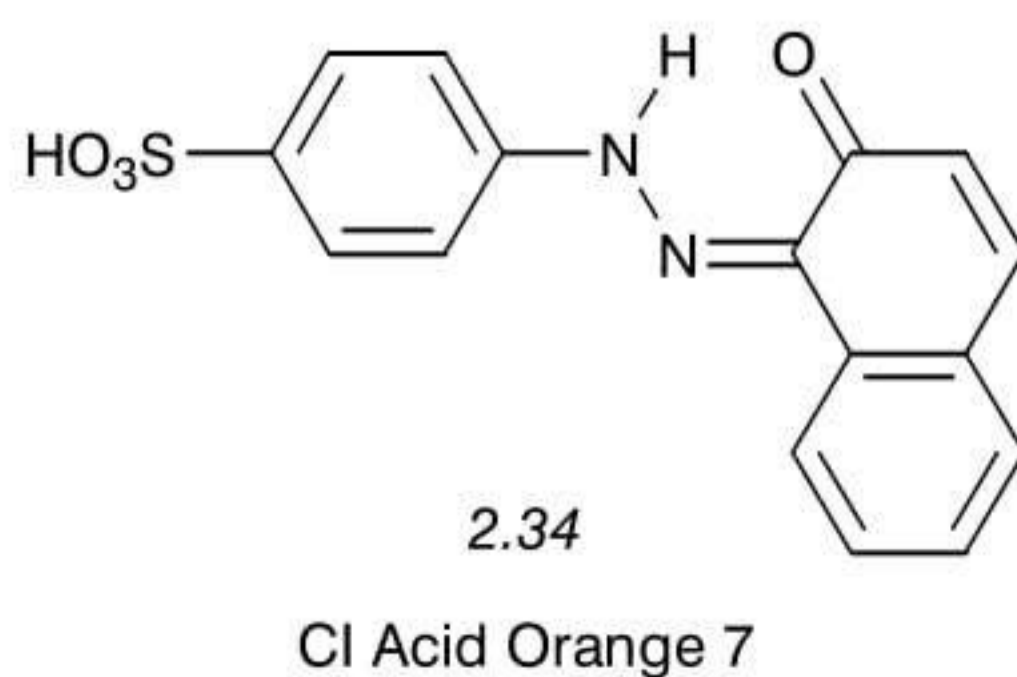
exchange has occurred. The amount of rosin soap used comprises some 15–30% of the mass of the final pigment.

Rosin acts as a non-diluting substrate and has the effect of increasing the proportion of particles in the pigment with a size below 250 nm, but there is no evidence of chemical combination. Attempts to fractionate rosin to identify any specially active constituent have been unsuccessful, as have attempts to find better general dispersing agents, although various manufacturers have produced ranges of easily dispersible pigments containing other additives. Preparations of crude CI Pigment Yellow 13 (2.20), the recrystallised material and the rosin-coated pigment were compared recently using solid state NMR spectroscopy and powder X-ray diffraction. The primary effect of rosination with either abietic acid or its derivative staybelite was to increase the crystalline order of the pigment [15].

Pigments in group 2b prepared from azo dyes

Many azo dyes prepared as sodium salts can be made into pigments by precipitating them as the salts of heavy metals, but only in the presence of basic substrates. The most commonly used substrate is alumina hydrate, as mentioned in section 2.2.1. The pigment is prepared by running solutions of the dye and a salt of the precipitating metal, generally barium or aluminium, into a suspension of alumina hydrate. An intimate mixture of the precipitated heavy-metal salt and alumina hydrate is formed and filtered off. The colloid chemistry of such systems, along with the technical and colour properties of the resulting pigments, is complex and depends on the dye: alumina hydrate ratio and the pH of the mixture. Weiser and Porter [16] studied the preparation of pigments from the dye Orange II (2.34; CI Acid Orange 7).

Many other dyes, including tartrazines and eosines, have been made into pigments in the past for use in printing inks, in which their soft texture and bright hues were much valued. Their light fastness was generally only 1 on the ISO scale and they are now obsolete.

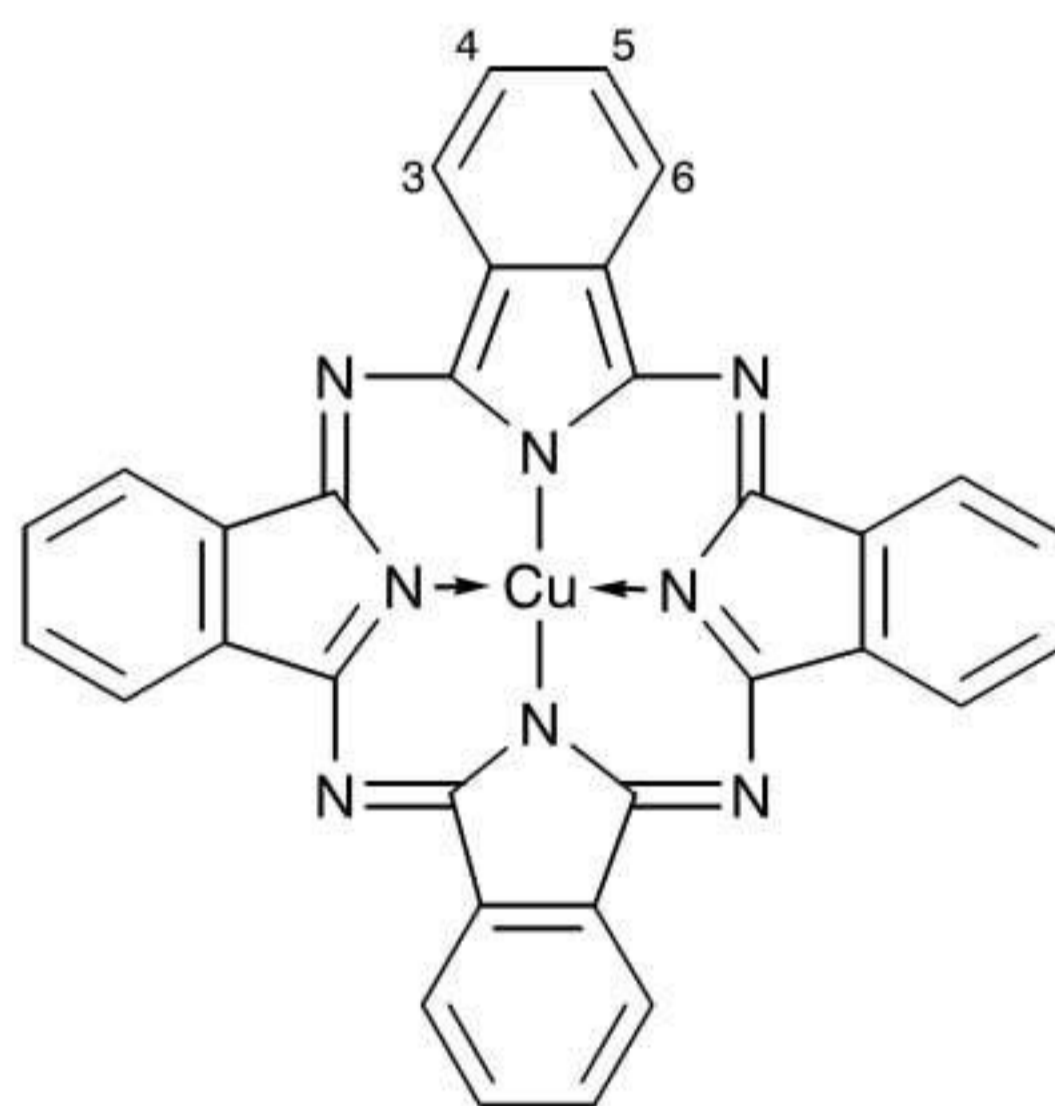


2.4 PHTHALOCYANINE PIGMENTS

Phthalocyanine was the first new chromogenic type to be introduced into the field of the colour chemistry of organic compounds concerned with pigments. Before this discovery, all the known organic pigments had been developed either by making dyes insoluble or by synthesising new insoluble azo compounds. This development is therefore interesting both technically and scientifically.

It began in 1928 when a blue impurity was found in phthalimide during its manufacture at Scottish Dyes (later part of ICI). The method of preparation being used was to pass ammonia through molten phthalic anhydride in an iron vessel [17]. It is now known that the blue impurity was iron phthalocyanine. This was found to be exceptionally stable and steps were taken to determine its structure. It is of interest that another important blue pigment (ultramarine; section 2.10.2) was also first synthesised as the result of investigating a blue impurity. This was in an industry not directly related to colour making, namely, sodium carbonate manufacture at St Gobain in France.

With hindsight it can be guessed that other ways of solving the impurity problem in making phthalimide, such as the use of a ceramic vessel, might well have solved the initial difficulty but would have resulted in missing the discovery of what has turned out to be a most important chromogen. Two other preparations of phthalocyanine had already been reported in the chemical literature but did not lead to the recognition of its usefulness, the first in 1907 [18] and the second in 1927 [19]. Linstead and his co-workers investigated the chemical structure of the blue impurity and its novel structure was finally established by Robertson [20] using X-ray diffraction. Copper phthalocyanine (2.35; CI Pigment Blue 15) first appeared commercially in 1935 under the ICI trade name of Monastral Blue B.



2.35

Copper phthalocyanine

2.4.1 Manufacture of copper phthalocyanine [21,22]

Two processes have been used for making copper phthalocyanine, but neither yields a form suitable for immediate use as a pigment since the physical form and size distribution of the resulting particles are far from the optimum. The product is generally referred to as 'crude blue' and requires purification and a sometimes complex series of finishing processes before it is in a form ready for use as a pigment.

The solvent process

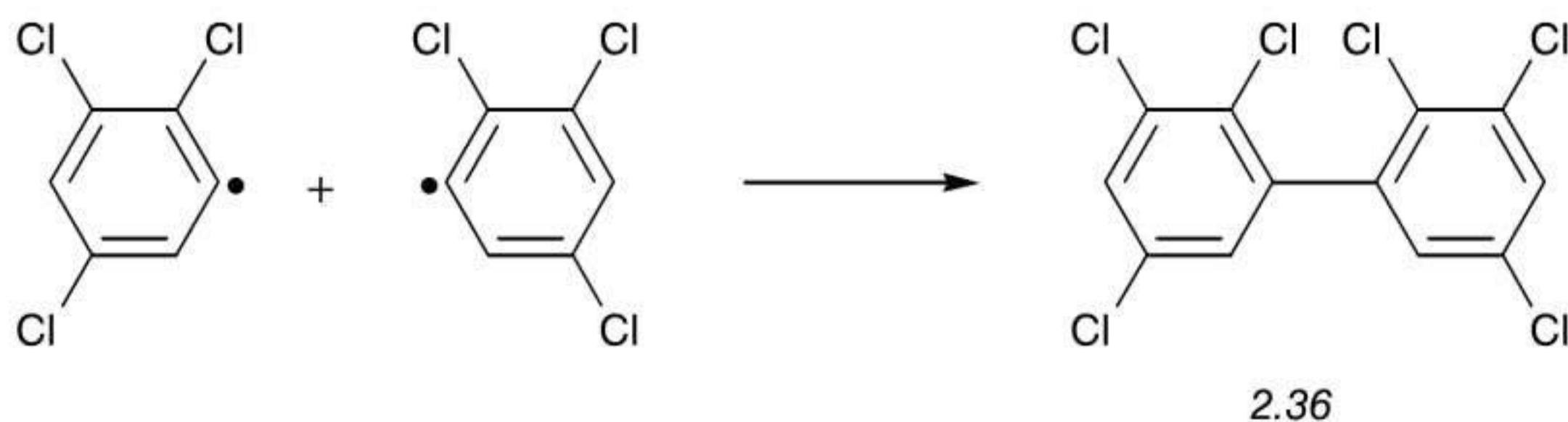
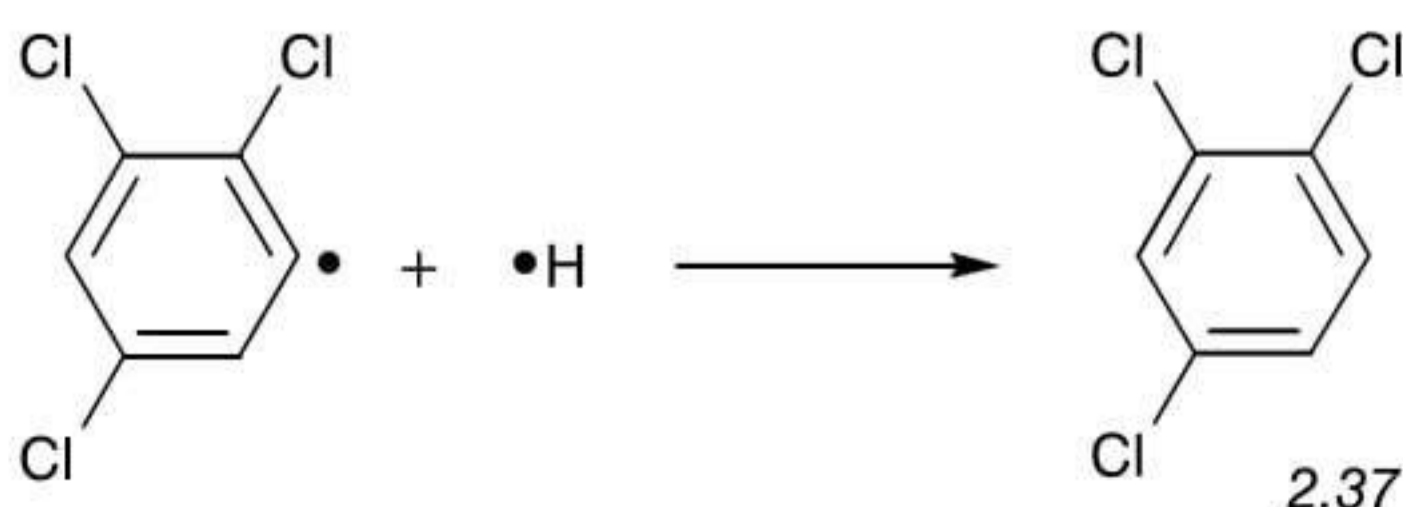
The reactants are phthalic anhydride, urea and copper(II) chloride, which are heated in a high-boiling aromatic solvent such as 1,2,4-trichlorobenzene, nitrobenzene or *m*-dinitrobenzene in the presence of a catalyst, usually ammonium molybdate. The solvent also acts as a heat-transfer medium. On heating to 120 °C an exothermic reaction begins and this temperature is maintained for about an hour. The temperature is then raised to 160–180 °C and kept constant for 6–12 hours. During this time ammonia and carbon dioxide are evolved, together with some solvent; the reaction is complete when ammonia evolution ceases. The remaining solvent is then removed by either steam or vacuum distillation. The yield is 90–95%. For many years the solvent process was in almost exclusive use.

Dry bake method

As the name implies, no solvents are used in this process and the expensive solvent recovery stage is not needed. Instead of phthalic anhydride, the more expensive phthalonitrile is used as reactant. Urea is not necessary as a source of nitrogen but seems to have been used by some manufacturers. The copper needed comes from copper(I) chloride. Continuous processing on moving heated copper belts has been attempted, but there were mechanical difficulties in handling the reactants and products after hard solid masses had formed. This problem was only partly solved by adding neutral inorganic diluents such as sodium sulphate or common salt to improve the fluidity. Interest in the dry bake process was renewed when polychlorobiphenyls (PCBs) were recognised as carcinogens and detected in crude blues produced by the solvent process.

Carcinogenic by-products

The mechanism of formation of PCBs from the trichlorobenzene solvent involves hydrogen abstraction by the urea present, leading to the formation of trichlorophenyl radicals. Two such radicals can then combine (Scheme 2.2) to form a PCB molecule (2.36). This reaction can be suppressed by adding antioxidants such as hydroquinone or sodium phosphite to yield hydrogen (H•) radicals, which convert (Scheme 2.3) the trichlorophenyl radicals back to the parent substance (2.37).

**Scheme 2.2****Scheme 2.3**

Other high-boiling solvents such as nitrobenzene and 2-nitrotoluene can also be used in the solvent process, but 4-nitrobiphenyl, a listed carcinogen, is produced when nitrobenzene is employed. One way to avoid the formation of substituted biphenyls is to employ a polysubstituted toluene as solvent, the substituents being chlorine or alkyl groups, mainly propyl. These are difficult to prepare but they have been patented by Toyo Inks.

Another approach is to use high-boiling aliphatic solvents with minimal aromatic content; boiling points are in the range 150–250 °C. Much higher ratios of solvent to reactants are needed than when aromatic solvents are used, owing to the high viscosity of the system.

Yet another method of avoiding PCB formation in the solvent process is to dispense with the need for urea as a reactant by using the more expensive phthalonitrile instead of phthalic anhydride.

Isolation of crude blue

No method of synthesis produces crude blue in pigmentary form. The solvent (if any) and the impurities must first be removed. Vacuum or steam distillation is used to remove the solvent, the former being generally cheaper. Impurities can then be removed by thorough washing for about two hours at 90–95 °C, first with 10% aqueous sodium hydroxide solution and then with 10% aqueous hydrochloric acid, followed by filtration, pressing, water washing and drying. From the purified crude blue, the copper phthalocyanine blue pigment is isolated in either the α - or β -crystal form. By introducing halogeno substituents into the molecule a series of green pigments can be derived (section 2.4.2).

Conversion of crude blue into copper phthalocyanine blue pigments

Purified crude blue exists in the most stable crystal form of copper phthalocyanine, the β -form, but the particles are much too large to make a good pigment. The β -form was that prepared by Robertson [20], from which he proved the molecular formula as mentioned earlier. Three other crystal forms of copper phthalocyanine have been reported but only one of them, the α -form, is of interest in the pigment industry. Mixtures of α - and β -forms have caused various technical problems because the former is reddish blue and the latter is greenish blue. The α -form has a tendency to revert to the more stable β -form in the presence of the organic solvents that are constituents of many paint formulations, with a consequent shade change and sometimes a loss of colour strength. Hence there is a need to prepare solvent-stable α -form pigments. Since β -form crystals also tend to grow and lose strength in the presence of organic solvents, there is a need to render them solvent-stable too.

Methods for making both forms solvent-soluble were the subject of many patents and closely guarded industrial secrets, but much of the mystery was cleared up in two papers by Gerstner [23] and Smith and Easton [24] published in 1966, by which time X-ray diffraction, electron microscopy and disc centrifuge particle sizing methods had been brought to bear on the problem.

Converting the β -form to the α -form

The β -form of crude blue can be converted to the α -form by complete disintegration of the crystals. This can be readily achieved by dissolving them in concentrated sulphuric acid,

thus forming a solution of single molecules, and then re-precipitating as α -form crystals by running the solution into a large volume of water. Careful control of the flow rate, coupled with stirring and temperature control (since heat is evolved in the process) and perhaps the presence of surfactants, can give tinctorially strong α -form pigments. Other methods, termed 'acid slurring' or 'permutoid swelling' involve the use of insufficient sulphuric acid to bring about complete solution. Copper phthalocyanine sulphate crystals are formed; these are then drowned in water as before, forming α -form crystals. Yet a third method of conversion is by prolonged salt grinding in a ball mill in the absence of any solvent. The α -form so produced, however, is not solvent-stable.

Solvent-stable forms

Smith and Easton [24] give the scientific basis of many of the patent claims. Salt grinding of either α - or β -form and treatment with solvent either during or after grinding gives the β -form. In the absence of solvent the product is the α -form, irrespective of the starting material. However, mixtures of α - and β -forms can result from salt grinding in the presence of solvent, depending on the grinding efficiency and the time of grinding in the mill. Two stages, first grinding and then solvent treatment, are often easier to control. For example, if the grinding process in the absence of solvent is stopped when about one-third of the material remains as the β -form, exposure to solvent will then cause a rapid reversion of the α -form back to the β -form, giving solvent-stable β -form. Solvent-stable α -form pigment can be made by incorporating some copper monochlorophthalocyanine in the pigment or by carrying out the salt grinding in the presence of compounds that can be adsorbed on the surface of the growing α -form crystals, hindering further growth and stabilising them against reversion to the β -form.

2.4.2 Other phthalocyanine derivatives

The discovery of the phthalocyanine chromogen gave rise to much research, particularly in view of its outstanding fastness properties. Many other metallic derivatives have been prepared and many substituents introduced into the phthalocyanine nucleus. Sulphonation has given some soluble dyes, which have even been converted back into pigments by making them insoluble again as barium salts. The only widely produced colorants are a range of green pigments made by halogenating copper phthalocyanine using chlorine either alone or mixed with bromine.

There are 16 hydrogen atoms on the benzenoid rings of the phthalocyanine molecule (2.35) that can in theory be replaced by halogens. Those in the eight 3,6-positions can be replaced easily whereas more severe conditions are needed for substitution in the 4,5-positions. The products of different manufacturers vary in the chlorine content, 14 or 15 atoms per molecule being usual in pigments under the generic name CI Pigment Green 7. As the number of chlorine atoms increases, the green pigments become increasingly yellow in hue. This trend can be carried still further by using mixtures of chlorine and bromine containing increasing amounts of bromine. The yellowest pigments have twelve bromine and two chlorine atoms per molecule and carry the generic name CI Pigment Green 36.

Direct chlorination of copper phthalocyanine can be carried out by passing the gas into a molten eutectic of aluminium chloride and sodium chloride at a temperature of 180–200 °C,

the copper phthalocyanine content being about 20% of the eutectic by mass. Iron(III) chloride is present as a catalyst [25]. Other methods include:

- chlorination in trichlorobenzene at 200 °C using 10% antimony trisulphide as a catalyst;
- chlorination under a pressure of 5–10 atmospheres at a lower temperature of 160–170 °C, a process in which the release of hydrogen chloride gas is used to control the pressure; and
- dry chlorination in a fluidised bed.

Yet other processes have used sulphuryl chloride (SO₂Cl₂), thionyl chloride (SOCl₂) or sulphur dichloride (SCl₂) as chlorinating agents.

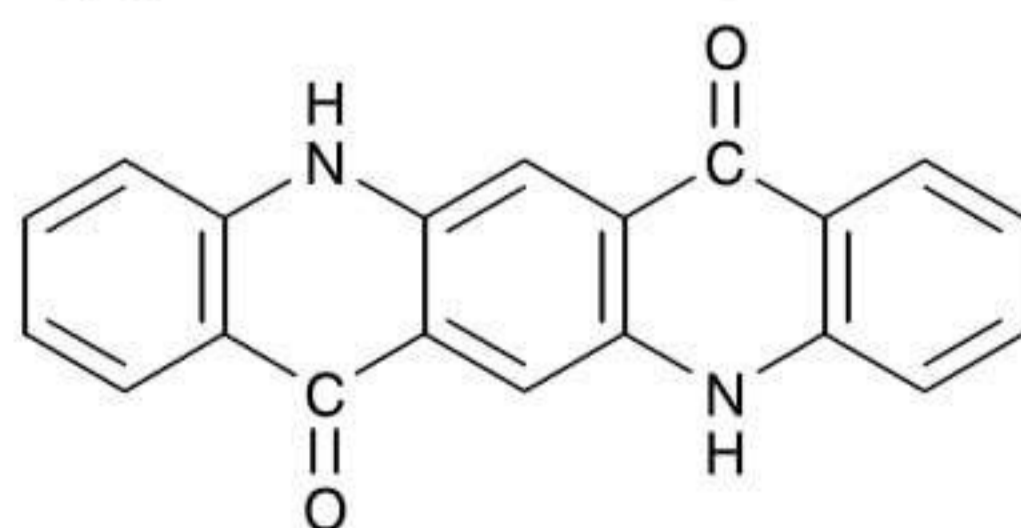
The crude polychlorinated copper phthalocyanine requires a finishing process to develop the full potential colour strength, but the problems are less than those experienced with copper phthalocyanine itself, as no problems of polymorphism occur. Finishing is carried out by acid pasting of the crude green in oleum or chlorosulphonic acid. The crystallinity, as shown by the sharpness of the X-ray diffraction pattern, can be improved by solvent treatment as there is no tendency for this to cause crystal growth. The light fastness rating (ISO 8) and solvent resistance (generally 5) are both as high as those of phthalocyanine blues, making them exceptionally high-quality pigments.

A great deal of research has been carried out to try to find organic pigments of red colour to match phthalocyanines in these two fastness requirements. The many red azo pigments show much inferior light fastness in reductions with titanium dioxide. Pigments made from vat dyes, mentioned earlier, have met the need to some extent, but there is still a gap in the organic colour pigment range for brilliant reds of the highest fastness properties.

2.5 QUINACRIDONE PIGMENTS

The synthesis of linear *trans*-quinacridone (2.38) was reported in 1935 by Liebermann [26] and was cursorily looked at as a red vat colorant but not developed commercially. It was more than twenty years later that the DuPont company introduced these compounds as pigments under the trade name of Cinquasia. Their chemical structures are based on CI Pigment Violet 19 (2.38). As with the phthalocyanines, this compound can exist in several polymorphic forms; in this case there are three, termed α -, β - and γ - forms; only the last two being useful as pigments. The first three pigments were called Cinquasia Red B (γ -form, size above 1000 nm), Cinquasia Red Y (γ -form, size below 1000 nm) and Cinquasia Violet R (β -form).

Quite apart from the problems of chemical synthesis, it is clear that the application of physico-chemical methods to pigment manufacture, first needed in the development of the



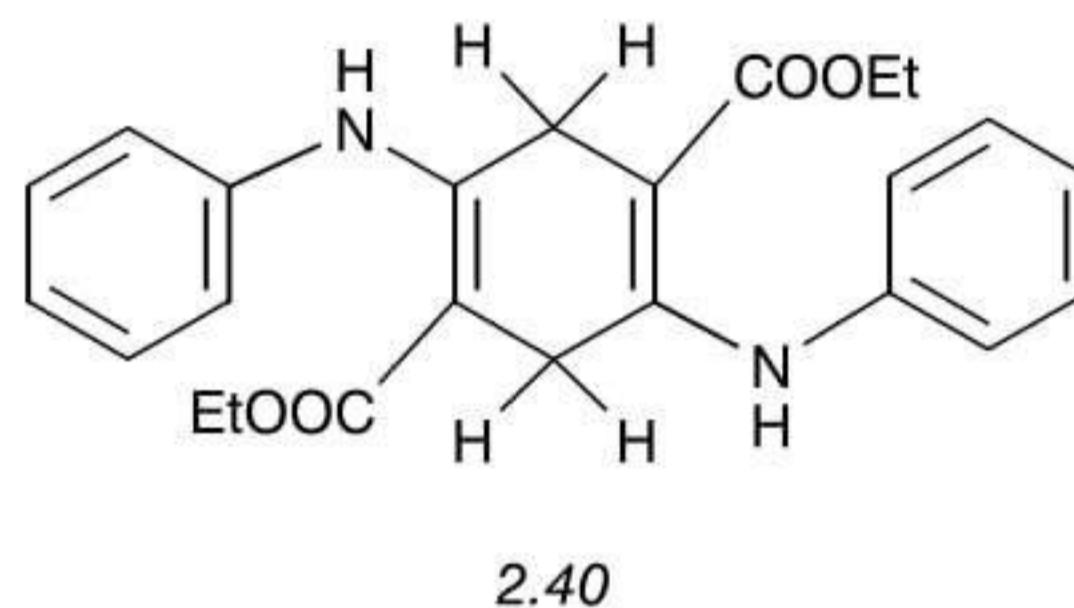
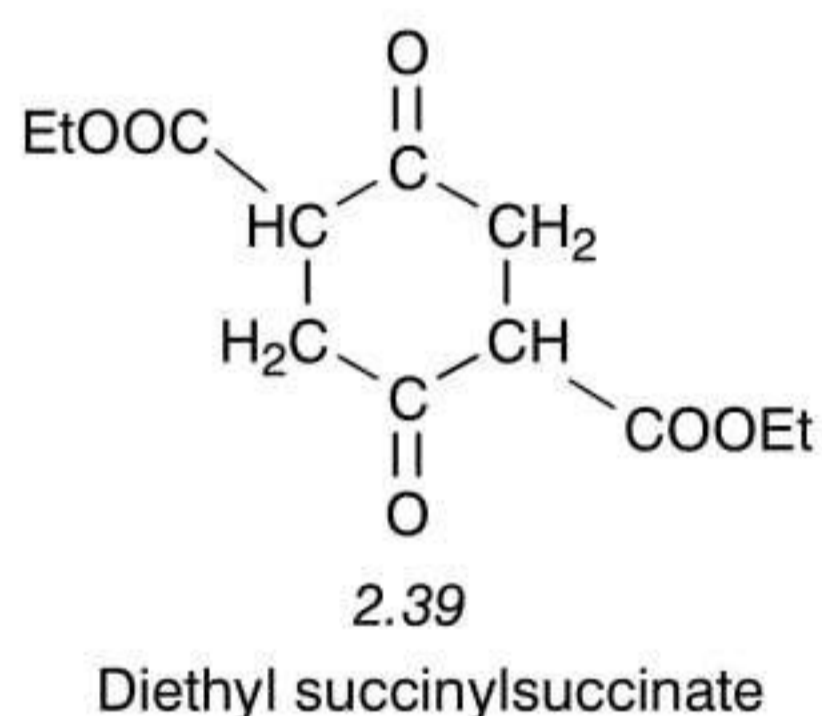
2.38

CI Pigment Violet 19

phthalocyanines, was essential to the successful introduction of these new pigments. X-ray diffraction methods are needed to recognise the crystal forms. The β -form was made from the crude product as synthesised by milling with a large amount of salt in the presence of xylene, whilst preparation of the γ -form required wet milling with dimethylformamide, followed by removal of the solvent and the salt with aqueous acid. Since the Red B and Red Y pigments differed only in their particle size, methods capable of measuring particles less than 1000 nm in diameter were obviously necessary. Such methods were not yet available in 1958 when DuPont first marketed these products.

The chemical synthesis of linear *trans*-quinacridones and their substituted derivatives that have been marketed subsequently is a complicated multi-stage sequence, making such pigments very expensive and sustainable only where high-fastness red pigments are essential, as in the car industry. There are four routes of synthesis, details of which have been given by Pollack [27].

The DuPont company used the succinic acid ester process, in which diethyl succinate is first cyclised to diethyl succinylsuccinate (2.39) in a sodium/alcohol mixture. One mole of the product is next condensed with two moles of aniline under oxidising conditions, forming diethyl 2,5-dianilino-3,6-dihydroterephthalate (2.40). Ring closure at 250 °C gives dihydroquinacridone, from which quinacridone is obtained by oxidising away the two extra hydrogen atoms.

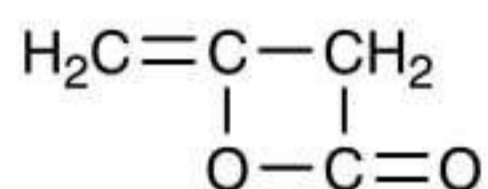


The Sandoz company used the dibromoterephthalic acid method. This acid was made from *p*-xylene by brominating it to form 2,5-dibromo-*p*-xylene and then oxidising this to 2,5-dibromoterephthalic acid. Reaction of one mole of this acid with two moles of an arylamine in the presence of copper(II) acetate gives 2,5-bis(arylamino)terephthalic acid, which can be ring-closed to a linear quinacridone. Unsymmetrical substitution using two different arylamines is possible.

The BASF route started from hydroquinone, which was converted to 2,5-dihydroterephthalic acid by a Kolbe-Schmitt reaction. One mole of this acid was treated with two moles of an arylamine, both components being in the form of a suspension in aqueous methanol. This was added to a small amount of a solution of vanadium(III) chloride and sodium chlorate. Gentle heating gave a 95% yield of 2,5-bis(arylamino)benzo-1,4-quinone-3,6-dicarboxylic acid. Ring closure to the *trans*-quinacridonequinone took place in the presence of concentrated sulphuric acid at 60–80 °C. This was then reduced to the required crude pigment by zinc or aluminium powder in caustic soda under pressure, in an aluminium chloride/urea melt or by the use of a sulphuric acid/polyphosphoric acid mixture.

The fourth synthesis, developed by the Swiss Lonza company and known as the diketene process, resembles the succinic acid ester process of DuPont in that the central ring of the

quinacridone molecule is totally synthesised. Acetone vapour is passed over an electrically heated wire to form first ketene, $\text{H}_2\text{C}=\text{C}=\text{O}$, which then dimerises to form diketene (2.41). Chlorination in the presence of alcohol yields ethyl 4-chloroacetoacetate, $\text{ClCH}_2\text{COCH}_2\text{COOEt}$. This reaction proceeds at low temperature but is exothermic to a considerable extent and can only be successfully carried out on a large scale in special reactors having an extensive surface area. Diketene also reacts with aromatic amines to yield acetoacetanilides, which are the coupling components needed to prepare Hansa Yellows (Table 2.4).



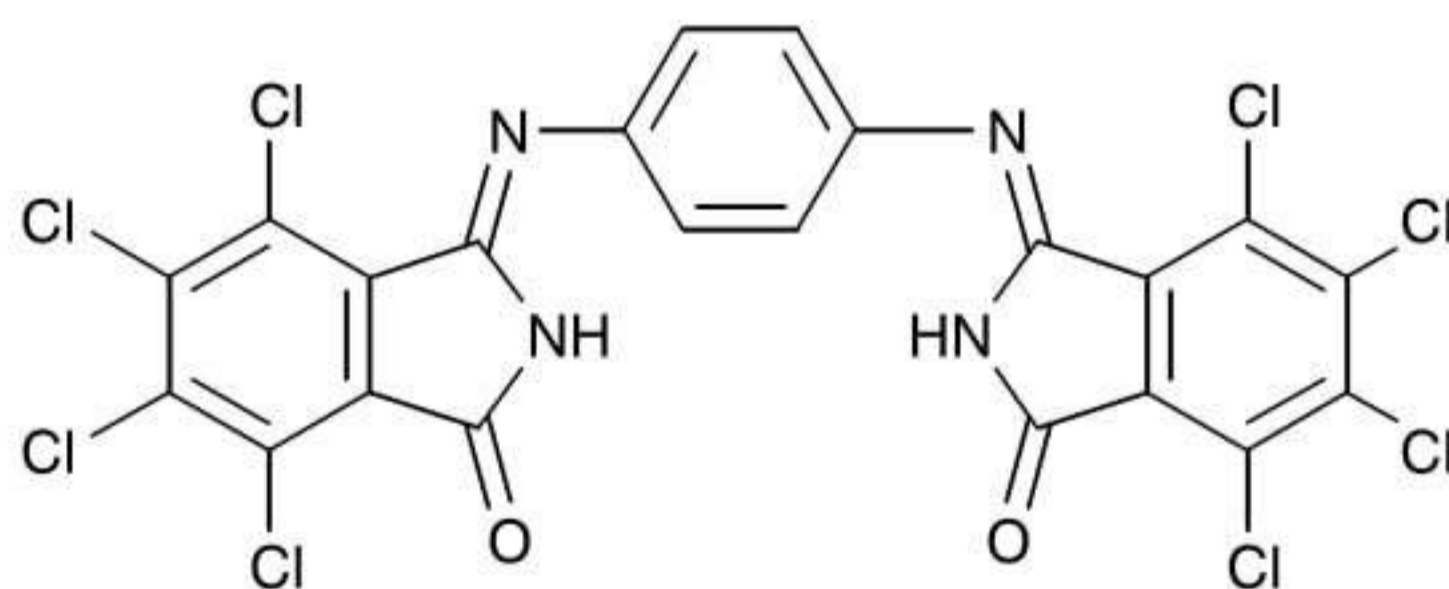
2.41

Diketene

In the manufacture of quinacridone pigments only the first and last of the four routes outlined have been operated commercially. Synthesis is followed by the milling processes necessary to give products with the crystal structure and particle size required for their use as pigments.

2.6 ISOINDOLINONE PIGMENTS

Another new chemical class of pigments, called Irgazins, was produced in 1964 by the Geigy company [28]. These products are made by condensing two moles of 4,5,6,7-tetrachloroisoindolin-1-one with one mole of an aromatic diamine. Thus *p*-phenylenediamine gives the yellow pigment CI Pigment Yellow 110 (2.42), which has high light fastness and heat resistance. The analogous CI Pigment Yellow 109 derived from 2-methylphenylene-1,4-diamine is greener in hue. Both of these pigments are used in plastics coloration, particularly of polyolefins.



2.42

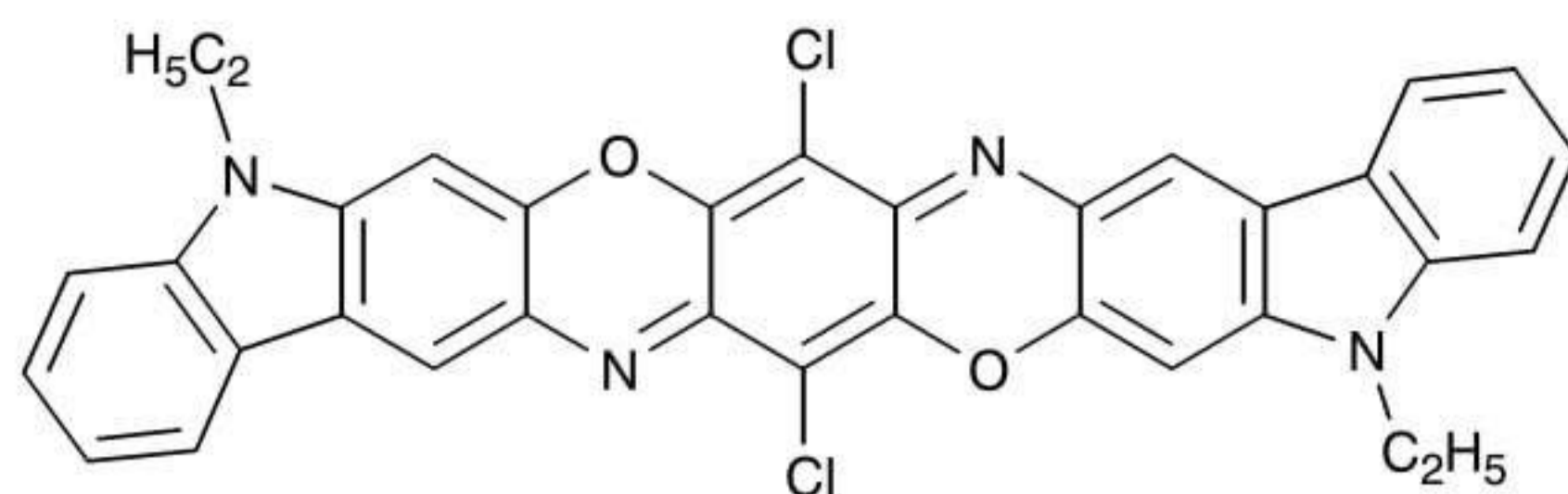
CI Pigment Yellow 110

2.7 DIOXAZINE PIGMENTS

Triphenodioxazine compounds have been used to make brilliant blue direct and reactive dyes for cellulosic fibres, but only one pigment in this chemical class, CI Pigment Violet 23 (2.43), is widely used. It is prepared by condensing 3-amino-9-ethylcarbazole with chloranil in trichlorobenzene [29]. As with many other pigments, manufacturers offer it in many physical forms adapted to the intended end-use.

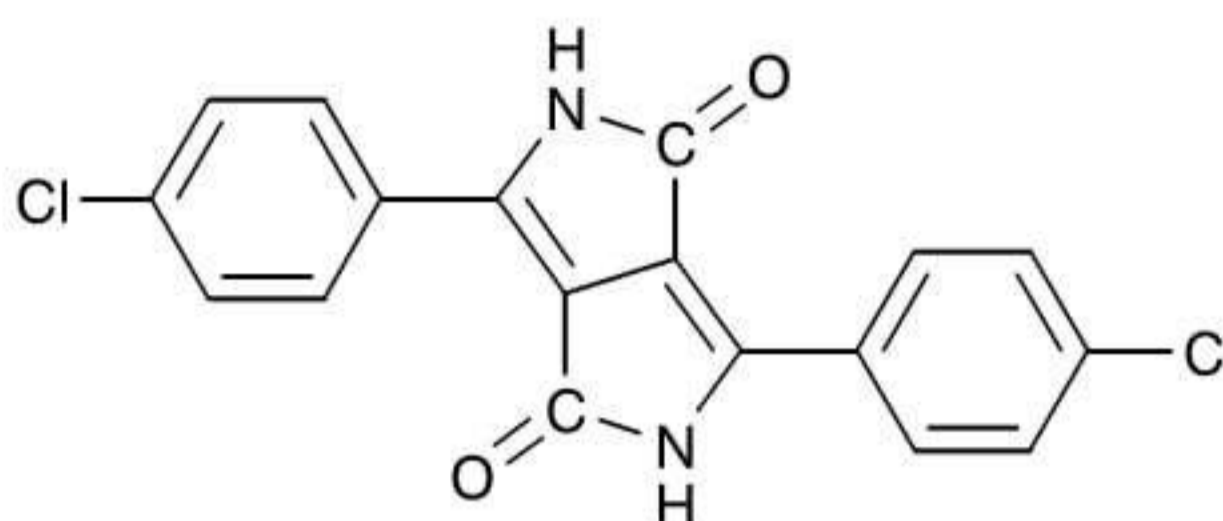
2.8 DIKETOPYRROLOPYRROLE PIGMENTS

This novel brilliant red chromogen was discovered by Iqbal and Cassar of Ciba-Geigy in 1983. It has yielded several useful derivatives with first-class application and fastness



2.43

CI Pigment Violet 23



2.44

CI Pigment Red 254

properties in this region of the colour gamut [30]. A typical example is the dichlorinated compound CI Pigment Red 254 (2.44).

2.9 FLUORESCENT PIGMENTS

A colorant of this type is not a pigment in the same sense that has been used so far in this chapter, that is, essentially a single chemical compound that can be used to colour media in which it is not soluble. Fluorescent pigments are based on fluorescent dyes which are soluble in certain resins. A resin coloured in this way is ground to a powder of small particle size and this 'fluorescent pigment' is dispersed into various media in the same way as other pigments. The molecular mechanism by which dissolved dye exhibits fluorescence is discussed in section 11.2. The overall result is that the paints, printing inks and plastics into which fluorescent pigments have been incorporated have vivid bright colours which attract the eye. This property is very valuable for safety clothing worn by police, rescue workers and others working in hazardous situations. Their vehicles also become much more visible when parts of them are painted with special finishes containing these colorants. Other uses include advertising and plastic toys.

The resins used to make fluorescent pigments are usually toluenesulphonamide-melamine-formaldehyde matrices. The dyes used for this purpose include CI Disperse Yellow 11, Rhodamine 6G (CI Basic Red 1) and Rhodamine B (CI Basic Violet 10). More details of the fluorescent dyes used have been given in a review by Christie [31].

Unfortunately, the fluorescent effect is not directly proportional to the concentration of colorant present, since there is considerable quenching if quite low concentrations are exceeded. The light fastness of the fluorescent pigments is also less than that of many other organic pigments now available, but improvement can be achieved using overlayers containing ultra-violet absorbers. This is an area in which further research will clearly be needed.

2.10 INORGANIC PIGMENTS

Inorganic pigments have a special place in pigment chemistry for several reasons. Some are cultural and historical. The art galleries of the world are filled with oil paintings in which the colours were, until the industrial revolution, produced entirely from mixtures of inorganic pigments obtained from natural sources, the so-called earth pigments. Later some of these were made industrially.

Another reason for the importance of inorganic pigments is that there are no white organic pigments. White pigments are essential to provide opacity to the paints and printing inks used on metal, wood, paper, textile fabrics and plastic films. White inorganic pigments are also used to provide opacity to synthetic fibres and the vast numbers of articles made from plastics by moulding and extrusion processes. The term plastics covers a whole range of different polymers, including polyamides, polyesters, ABS (acrylonitrile-butadiene-styrene) copolymers, poly(vinyl chloride) and polyolefins. The uses to which these plastics are put, their different physical and chemical properties, and the technologies used in fabricating them sometimes including the use of quite high temperatures, impose stringent demands on any colorants used in them. Inorganic pigments, both white and coloured, can generally meet these demands more often than organic pigments. There are no general rules which apply and the only way to find out which individual pigments are suitable is by practical trials. In uses where high light and weathering fastness is required, such as in paint for cars, many organic pigments do not meet the required standards. Inorganic pigments are the only ones capable of withstanding the very high temperatures used in the manufacture of glass and in the glazing of pottery after it has been decorated.

Carbon black in one of its many forms is the colorant most widely used in printing inks. Vast amounts are also used in formulating rubber for vehicle tyres, where the carbon black also plays an important part in the vulcanisation process when rubber is hardened by reacting it with sulphur during manufacture of the tyres. The primary criteria for carbon black selection in fibre coloration are colour and undertone, but secondary properties must match the final application. Carbon black performance is determined by prime particle size and aggregate structure. Inconsistent dispersion performance may arise by sub-optimal compounding leading to poor dispersion of the carbon black agglomerates, or from low-quality carbon black containing undispersible contaminants. Recent quality improvements include a new carbon black for increasing the lifetime of continuous filters and close control of residual impurities improving carbon quality in black-pigmented polyester film used in food packaging [32].

A recent survey of the technical and environmental aspects of inorganic pigments by Schwarz and Endriss [33] has put the importance of these products into numerical perspective. Of a total worldwide production of some 5M tonnes of pigments, 96% are inorganic. Of this 4.8M tonnes, carbon black and various whites account for 84%, that is just over 4M tonnes. This means that world production of coloured inorganic pigments is approximately 0.8M tonnes.

2.10.1 White inorganic pigments

The primary requirement for a compound to be of a white appearance is that it should not absorb any of the radiation in the visible part of the electromagnetic spectrum, that is, of wavelengths between 400 and 650 nm; in practice this is seldom attainable and slightly less

than 100% transmission can be tolerated, but there must be no marked absorption bands. The additional requirement for a substance to be usable as a white pigment is that it should have as high a refractive index throughout the visible spectrum as possible. A third criterion is that it should be in the form of particles fairly uniform in size, with diameters of the order of 1000 nm.

Because pigments are used as dispersions of particles in media of a refractive index of about 1.5, this is the lower limit for their practical use. There are several white inorganic compounds with refractive indices between 1.5 and 1.63 which are called 'transparent whites' or 'extenders'. These include whiting (CaCO_3 ; CI Pigment White 18), china clay (CI Pigment White 19), barytes (BaSO_4 ; CI Pigment White 22), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; CI Pigment White 25), talc and silica. These compounds confer very little opacity and are mainly used to thicken the paints into which they are incorporated.

White pigments, some of rather variable composition, that have been used in the past include white lead (CI Pigment White 1), refractive index 1.9; zinc oxide (CI Pigment White 4), r.i. 1.9; lithopone (CI Pigment White 5), r.i. 1.84; zinc sulphide (CI Pigment White 7), r.i. 2.3; antimony oxide (CI Pigment White 11), r.i. 2.2. All have been eclipsed by titanium dioxide (CI Pigment White 6).

Titanium dioxide

As a pigment this is used in two crystalline forms: rutile (r.i. 2.71) and anatase (r.i. 2.51). It is these high refractive indices which, combined with modern manufacturing methods, have ensured its pre-eminence.

The ore used for making commercial titanium dioxide is the black ilmenite, nominally $\text{FeO} \cdot \text{TiO}_2$ but containing small amounts of many impurities, depending on the source. The development of manufacturing methods to prepare pure titanium dioxide in the form of either rutile or anatase took many years. Anatase pigments appeared in the mid 1930s and rutile pigments in the 1940s. One of the problems was to remove the last traces of iron and other metallic impurities which distorted the crystalline lattice, leading to inferior whiteness.

There are now two processes in widespread use for making titanium dioxide pigments. In the sulphate process, finely ground ilmenite is digested in sulphuric acid and the iron is reduced and separated as iron(II) sulphate. The titanium(IV) sulphate is hydrolysed by steam to a hydrous oxide, which is thoroughly washed to remove soluble impurities and finally calcined at a temperature of about 1000 °C to give the anatase form of titanium dioxide.

In the chloride process, developed in about 1960, the titanium in the ore is converted to titanium(IV) chloride by heating it to 800 °C with chlorine in the presence of carbon, which combines with the released oxygen. The purified chloride is then oxidised to titanium dioxide at 1000 °C and the chlorine formed is recycled. Technical problems arise because the oxidation of titanium(IV) chloride is not sufficiently exothermic to make the reaction self-sustaining but these can be overcome by pre-heating the reactants and by burning carbon monoxide in the reactor to raise the temperature. By careful control of the conditions, it is possible to produce pure rutile particles of a mean size of 200 nm.

Titanium dioxide is non-toxic, in marked contrast to pigments such as white lead, and is widely used as a pigment in utensils and on surfaces coming into contact with food in industry, as well as in almost all other uses calling for white pigment. It is not the easiest

pigment to disperse and, after a long struggle to produce it in pure form, most manufacturers now produce a range of quite heavily coated forms, each prepared to facilitate and maintain dispersion in particular media.

Both crystal forms of titanium dioxide are photochemically active, anatase more than rutile. Under ultraviolet light the pigment releases active oxygen, which can tender textile fibres or degrade paint films, causing 'chalking'. In the dark, atmospheric oxygen regenerates the titanium dioxide and the cycle of degradation recurs. In applications where this is a major problem, rutile-form pigments containing additives such as antimony(III) sulphide are therefore used.

Much research had to be done during the development of large-scale processes to prepare titanium dioxide in two different crystal forms and in a high state of purity. The knowledge so gained has been put to good use and led to the production of several new coloured inorganic pigments. These products are based on the discovery that the rutile lattice can absorb certain metal oxides into its structure to give coloured pigments which retain the high fastness properties of pure titanium dioxide. These pigments are discussed in the next section.

2.10.2 Coloured inorganic pigments

During the first half of the 20th century, when linseed oil was the primary medium from which paints were made and phenol-formaldehyde resin was the basis of most plastic materials, both paints and plastics were usually coloured using inorganic pigments. The second half of the century saw the introduction of many new types of plastics and the annual world production of them rose above the 100M tonnes mark. Much of this had to be coloured for identification or decorative purposes. The simplest way to do this is to colour the whole of the plastic before extruding or moulding it into the shape of the finished article, rather than to apply a coloured surface coating later. Whilst some of the pigment was no doubt wasted by being buried in the interior, this loss was completely outweighed by the economy of a single-step operation to the required finished article and uniformity of colour between separate batches.

The result was a big increase in the demand for pigments which met the necessary fastness standards and withstood the heating involved. Many organic pigments could not meet these requirements and some of them adversely affected the moulding process itself, or the dimensional stability of the finished articles. Inorganic pigments, or mixed organic/inorganic products, overcame the problems in some instances, despite the less easy dispersibility of the inorganics. The coloured inorganic pigments in current production are generally those that have particular advantages which organic pigments cannot match.

Ultramarine

This is the synthetic form of the blue mineral lapis lazuli, which was imported from China and India in the Middle Ages. It is characterised by its attractive blue colour, high light fastness (ISO 7–8), excellent resistance to alkalis and all organic solvents, easy dispersibility and non-toxicity, but it has poor resistance to acids. It was first made by Guimet in France in 1830 after having been noticed as an impurity in the glass furnaces at St Gobain. It is now made by calcining a mixture of the ingredients shown in Table 2.5, which are first finely

ground and formed into bricks. The reaction takes 4–5 days in a sealed muffle furnace at 800 °C, during which time the sodium carbonate reacts with the alumina and silica to form a zeolite, a hydrated silicate of calcium and aluminium. This reacts with the sodium polysulphides formed at the same time to give primary green ultramarine. As the furnace cools, air diffuses into it and the primary green oxidises to form raw blue ultramarine. The oxidation process can be accelerated by blowing in sulphur dioxide. The product at this stage contains 20–25% sodium sulphate, which is leached out with water. The remainder is then ball-milled in the wet state until the size of the particles is in the range 500–6000 nm. The particles are next separated into size fractions by sedimentation or centrifugal methods. The coarsest fraction is used for laundry blues, the intermediate fraction in plastics coloration and the finest in high-grade printing inks.

Table 2.5 Ingredients used in the manufacture of ultramarine

Ingredient	Amount (%)
China clay	30
Sodium carbonate	32
Sulphur	30
Silica	4
Rosin	4

The formula as deduced from chemical and X-ray structural analysis is $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$. There is an open framework of SiO_4 tetrahedra with shared corners. Some silicon ions are replaced by aluminium ions, however, and to preserve electrical neutrality sodium cations are needed. These are in excess and the overall balance is maintained by the S^{2-} , S_2^{2-} and S_3^{2-} ions present. Consequently, chemical formulae containing fractional proportions of elements are possible.

The colour of inorganic compounds is associated with charge transfer within the structure. This can be brought about by specific light absorption, so that the variability of ultramarine composition that can be achieved opens up many possibilities for colour changes. Pure starting materials, particularly the absence of iron impurities, are necessary in making consistent pigments.

As well as the basic ultramarine with two sulphur atoms in its formula, which is CI Pigment Blue 29, two other pigments based on it are commercially available. These products are CI Pigment Violet 15 and CI Pigment Red 259, the latter having a pink colour. Both pigments are made from ultramarine by oxidation and ion exchange but have a lower colour strength.

The refractive index of these pigments is about 1.5, which means that they give a transparent blue when used in paints and clear plastics. Opacity can be increased by adding small amounts of titanium dioxide. The principal failing of ultramarine is its lack of resistance to acid, which can even decompose the pigment if there is sufficient available. Coated grades are made with substantially improved acid resistance.

Cadmium pigments

A range of mixtures containing cadmium sulphide and varying amounts of zinc sulphide or cadmium selenide can be made, the resulting colours being as shown in Table 2.6. The outstanding brilliance of shade of these pigments cannot be matched by any other inorganic pigment. Equally bright organic pigments have lower heat stability than have cadmium pigments, which can withstand temperatures of 400 °C. Other advantages of the cadmium pigments are better solvent fastness and high fastness to migration, particularly in plastics, including ABS, polyolefins and extended PVC.

Table 2.6 Colours obtainable with cadmium pigments

Colour	Components	CI Pigment
Primrose	CdS, ZnS	Yellow 35
Yellow	CdS	Yellow 37
Orange	CdS, 0.2 CdSe	Orange 20
Red	CdS, 0.4 CdSe	Red 108
Maroon	CdS, 0.7 CdSe	Red 108

The starting material for making these pigments is cadmium sulphate, which must be free from iron, nickel and copper impurities. Cadmium sulphide is precipitated from the sulphate solution by adding an alkaline solution of pure sodium sulphide under controlled conditions of pH, temperature and addition rate. The yellow product is in the cubic crystal form, which is converted into the required hexagonal form by calcination at 500–600 °C in the absence of air.

Primrose pigment containing zinc sulphide is made by adding zinc sulphate to the cadmium sulphate starting material and the zinc sulphide appears in solid solution in the final product. The pigments consisting of mixtures of cadmium sulphide and selenide are made rather differently. An alkaline slurry of cadmium carbonate is made by mixing solutions of cadmium sulphate and sodium carbonate. At the same time selenium is added to a solution of sodium sulphide to form sodium sulphoselenide as a source of S-Se polyanions. This must be kept alkaline to prevent the precipitation of selenium. Mixing of a solution of the correct composition with the cadmium carbonate slurry ensures the precipitation of cadmium sulphoselenide that will yield the desired hue. After washing, the precipitate is calcined to give the pigment.

Both cadmium and selenium are poisonous and there are regulations about the limits of free cadmium in the pigment (100 p.p.m.) and on the disposal of waste liquors from manufacturing plants.

As well as the uses in plastics already mentioned, these pigments are used in car paints and stoving enamels, and also in leather finishes and rubber.

Iron oxide pigments

Naturally occurring iron oxide pigments are widely distributed geographically and can be found in a wide range of colours from black to reds and yellows, depending on composition and crystal structure. Ochres of many kinds and from different sources were often used in oil

paintings by the Old Masters The use of magnetic iron oxides in recording tapes has stimulated their investigation at advanced technological level, but in the field of pigments their use has declined to that of cheap fillers for controlling paint flow properties and of facing colours for building bricks.

Iron(II) sulphate is a by-product in many industrial processes, such as the manufacture of titanium dioxide, the pickling of steel sheet before galvanising and the reduction of aromatic nitro compounds to amines using iron catalysts. Conversion of waste iron(II) salts to usable iron oxide pigments, where the quality requirements are not too stringent, is therefore a useful proposition, since it uses up chemicals that would otherwise be regarded as waste products.

Yellow iron oxides can be prepared by precipitating iron(II) hydroxide from a solution of iron(II) sulphate by adding sodium hydroxide and then bubbling air through the heated suspension to oxidise it to α -iron(III) oxide hydrate (α -FeOOH or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). An alternative method uses a single step of passing a mixture of air and ammonia into the iron(II) sulphate solution, followed by a heating stage. Seeding of the precipitated dispersion with a previously prepared pigment of the required crystal form helps to control the quality of the final product.

Red, brown and black iron oxides are prepared by first heating green iron(II) sulphate crystals to remove six of the molecules of water of crystallisation (leaving $\text{FeSO}_4 \cdot \text{H}_2\text{O}$) and then calcining the product to the desired form of iron(III) oxide with the evolution of sulphur oxides.

Currently produced iron oxide pigments are listed in Table 2.7. Similar pigments occur naturally in many parts of the world, but are of course mixed with other mineral substances.

The crystallography of iron oxides is complex because there are two oxides, FeO and Fe_2O_3 , as well as α -FeOOH, which can occur in mixed crystals. Kittel [34] has given a full account of the chemistry and Feitknecht [35] has discussed the theory of the colours of these pigments.

Table 2.7 Synthetic iron oxide pigments

Colour	Formula	CI Pigment
Yellow	FeOOH	Yellow 42
Red	Fe_2O_3	Red 101
Brown	Fe_2O_3 & $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ mixtures	Brown 6
Black	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$	Black 11

Lead Chromate pigments

This group of pigments includes chrome yellow, chrome orange and molybdate red (Table 2.8). Their colours range from lemon yellow to bluish red. The chrome yellow pigments are pure lead chromates or mixed-phase pigments of lead chromate and lead sulphate. Partial replacement of chromate by sulphate in the mixed-phase crystals causes a gradual reduction of tinting strength and hiding power, but allows production of chrome yellows with a greenish yellow hue [33]. Chrome orange pigments are basic lead chromates that vary in content of PbO and PbSO_4 . Molybdate red pigments are mixed-phase pigments containing lead chromate, lead sulphate and lead molybdate. Their colour depends on the proportion of molybdate, crystal form and particle size.

Table 2.8 Lead chromate pigments

Common name	Formula	CI Pigment
Chrome yellow	$\text{Pb}(\text{Cr},\text{S})\text{O}_4$	Yellow 34
Chrome orange	$\text{Pb}(\text{Cr},\text{S})\text{O}_4$	Orange 21
Molybdate red	$\text{Pb}(\text{Cr},\text{S},\text{Mo})\text{O}_4$	Red 104

The presence of lead and hexavalent chromium in these products is of chronic hazard concern and the EU has classified these pigments as harmful substances. Lead is soluble at stomach-acid concentrations and can accumulate in the organism. The results of a high lead intake include inactivation of enzymes and disturbances in the synthesis of haemoglobin. Hexavalent chromium compounds are considered to be carcinogenic. For these reasons the usage of lead chromate pigments has declined considerably in recent years.

Complex coloured inorganic pigments

There are two types of pigments in this category, rutile and spinel pigments. The first, as mentioned already in section 2.10.1, have been developed as a result of the research done to produce titanium dioxide in pigmentary form. By calcining pure rutile with nickel and antimony oxides at a high temperature, the rutile lattice becomes able to absorb about 3% of nickel(III) oxide and 10% of antimony(V) oxide. The first of these imparts a yellow colour and the second serves to maintain the overall valency of the cations at four. The characteristic properties of nickel and antimony oxides are no longer apparent after incorporation in the rutile lattice. The commercial product is designated CI Pigment Yellow 53. A buff pigment of this type can be made using chromium(III) oxide instead of nickel oxide [36]. In either of these products niobium oxide can be used instead of antimony oxide, giving a pigment of higher colour strength. Brown pigments are produced if manganese(III) oxide is used instead of nickel or chromium oxide in the calcination, an example being CI Pigment Brown 37.

Spinel minerals have the formula $\text{MO}\cdot\text{R}_2\text{O}_3$, where M is a divalent metal such as magnesium and R is a trivalent metal, for example aluminium. Blue pigments are obtained when the metals in the spinel $\text{MgO}\cdot\text{Al}_2\text{O}_3$ are partially or completely replaced by cobalt. Cobalt Blue is CI Pigment Blue 28 with the formula $\text{CoO}\cdot\text{Al}_2\text{O}_3$. The main uses of these pigments are in paints and in plastics, where their fastness properties are excellent. Their high-temperature stability is particularly useful in plastics.

Metallic pigments

Attractive metallic effects can be obtained by incorporating very thin, small flakes of aluminium, copper or copper/zinc alloys in otherwise transparent surface coatings. The metal flakes act as tiny mirrors within these paints, which are particularly effective on the curved surfaces of cars since the colour changes with the angle from which the surface is viewed. The orientation of the flakes within the paint film also changes the colour seen by the eye, so that careful dispersion of the metal components of the paint is essential.

Aluminium flakes are listed as CI Pigment Metal 1, whilst copper and copper/zinc alloys are CI Pigment Metal 2. The latter can give the appearance of gold in suitable formulations. The transparency of the surface coatings in which the metallic pigments give their best effect is achieved in formulations which use solvent dyes, rather than coloured pigments, as the principal colorants. However, adequate fastness of the entire coating must be the overriding consideration.

2.11 HOW PIGMENTS ACT AS COLORANTS

This chapter has been concerned mainly with the chemistry of making pigments but has also stressed the importance of preparing them in the correct physical form. In the case of those pigments which can be made in more than one crystal form, such as the anatase and rutile forms of titanium dioxide, this may mean that all the pigment should be in one form only. In others, a mixture of polymorphic forms may be required, and it is then necessary to ensure that the desired ratio of these forms is present.

With all pigments, the particle size distribution of the pigment as synthesised is the most important single factor in ensuring its optimum potential performance in use, but this potential can only be achieved if the particles are properly dispersed. To understand why particle size is so important it is necessary to look in some detail at the optical behaviour of tiny pigment particles dispersed in a transparent organic medium. The exact nature of this medium depends on whether the end-use is a paint, a printing ink or a plastic.

In the case of paints and printing inks, the initial preparations will be in the semi-solid state because solvents are needed both in the process of dispersing the pigment in the paint or ink medium and for application purposes. These solvents dry out after the paint or ink is applied. When making coloured plastic articles, both heating and solvents may be used to aid dispersion in the plastic medium as part of the moulding process. However, from the viewpoint of the optical properties in all of these pigment uses, what is most important is that each of these media has a refractive index close to 1.5.

Refractive index is strictly defined as the ratio of the velocity at which light travels in a vacuum to that at which it travels through the medium. For present purposes, it is a sufficiently close approximation to use the velocity at which light travels in air, rather than in a vacuum.

Figure 2.2 gives a simplified analysis, based only on the theory of geometric optics and ignoring the wave properties of light, of what happens when a single particle of a light-absorbing (coloured) pigment, embedded in a transparent medium, is struck by a ray of white light. The size of the particle is many times greater than the wavelength of visible light (400–650 nm) and its refractive index is greater than that of the medium, which is about 1.5.

At point A in Figure 2.2, a ray of white light enters the medium and its velocity diminishes, with the result that its path is bent towards the normal at this point. Snell's law of refraction states that the relation between the angles of incidence (*i*) and refraction (*r*) is given by Equation 2.1, where *n* is the ratio of refractive indices of the medium and air.

$$n = \frac{\sin i}{\sin r} \quad (2.1)$$

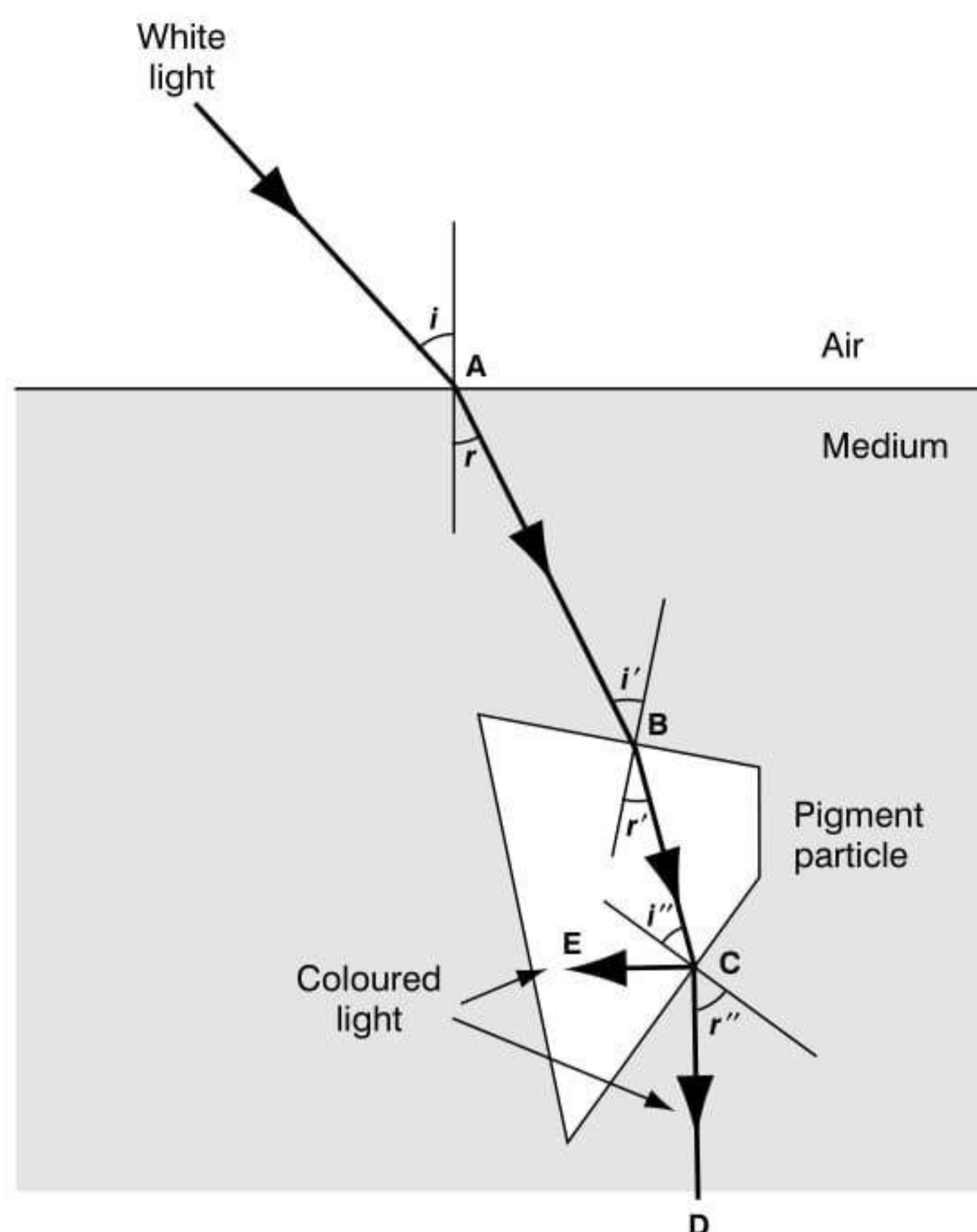


Figure 2.2 Optics of a single coloured pigment particle in a medium when struck by a ray of white light. The light becomes increasingly coloured as it travels from point B to point C

The ray then travels on in the medium and strikes the pigment particle at point B. Here it is again refracted and its path bent towards the normal. The relation between the angles i' and r' at point B is again given by Equation 2.1, but this time n is the ratio of refractive indices of the particle and medium, that of the particle being the greater. As the ray passes through the pigment particle some wavelengths of the light are absorbed. Which wavelengths these are and how much of them are absorbed, is determined by the shape of the absorption curve of the particular pigment involved. When the ray reaches the point C it will certainly be coloured to some extent, depending on the distance BC. At point C, one of two things may occur. If the angle of incidence i'' is smaller than the critical angle, the coloured light ray will emerge from the pigment particle and re-enter the medium, following a path CD with the angle r'' greater than i'' , as shown in Figure 2.2. If the angle i'' at point C is greater than the critical angle, however, total internal reflection will occur at that point and the ray will not emerge from the particle. The direction of travel of the ray will be effectively reversed and it will start on a path CE back through the particle and then possibly out into the medium and the air and thus to the observer's eye. Its exact path depends on the particle shape and its orientation in the medium. Which of these two possible paths the ray follows at point C depends on the value of the critical angle, Φ_c . This is given by Equation 2.2, where n_p and n_m are the refractive indices of the particle and medium, respectively. The important point is that the greater the refractive index of the particle, the greater is the chance of the critical angle being exceeded and the more light will start back towards the eye. A complete and detailed analysis would be very complicated, if not impossible, since in a real case lots of other particles, including those of different pigments, would be present.

$$\sin \Phi_c = \frac{n_p}{n_m} \quad (2.2)$$

If total internal reflection does occur at point C, the amount of absorption could be doubled. Too long a path within the particle, or a very high absorption coefficient, could mean that all the light is absorbed and the colouring power of the particle will thus be lost. This demonstrates one reason why the mean particle size of the coloured pigment must be arranged to minimise this possibility.

So far, the effect of light scattering has been ignored. Scattering occurs when light rays strike particles of linear size considerably less than the wavelength of visible light. What occurs is shown in Figure 2.3. The intensity of the scattered light is proportional to its incident intensity and also to the $1/\lambda^4$ power of its wavelength. Short-wavelength violet or blue light is scattered ten times more than red light. Incidentally, this explains why a clear sky in daylight appears blue, the scattering agent in such a clear sky being the molecules that form the atmosphere. This effect is, however, relatively unimportant in considering the optics of pigment particles dispersed in a medium. The most important points that follow from a consideration of the scattering phenomenon are that white pigments should

- (a) not significantly absorb visible light,
- (b) consist of particles of mean size well below the wavelength of visible light, and

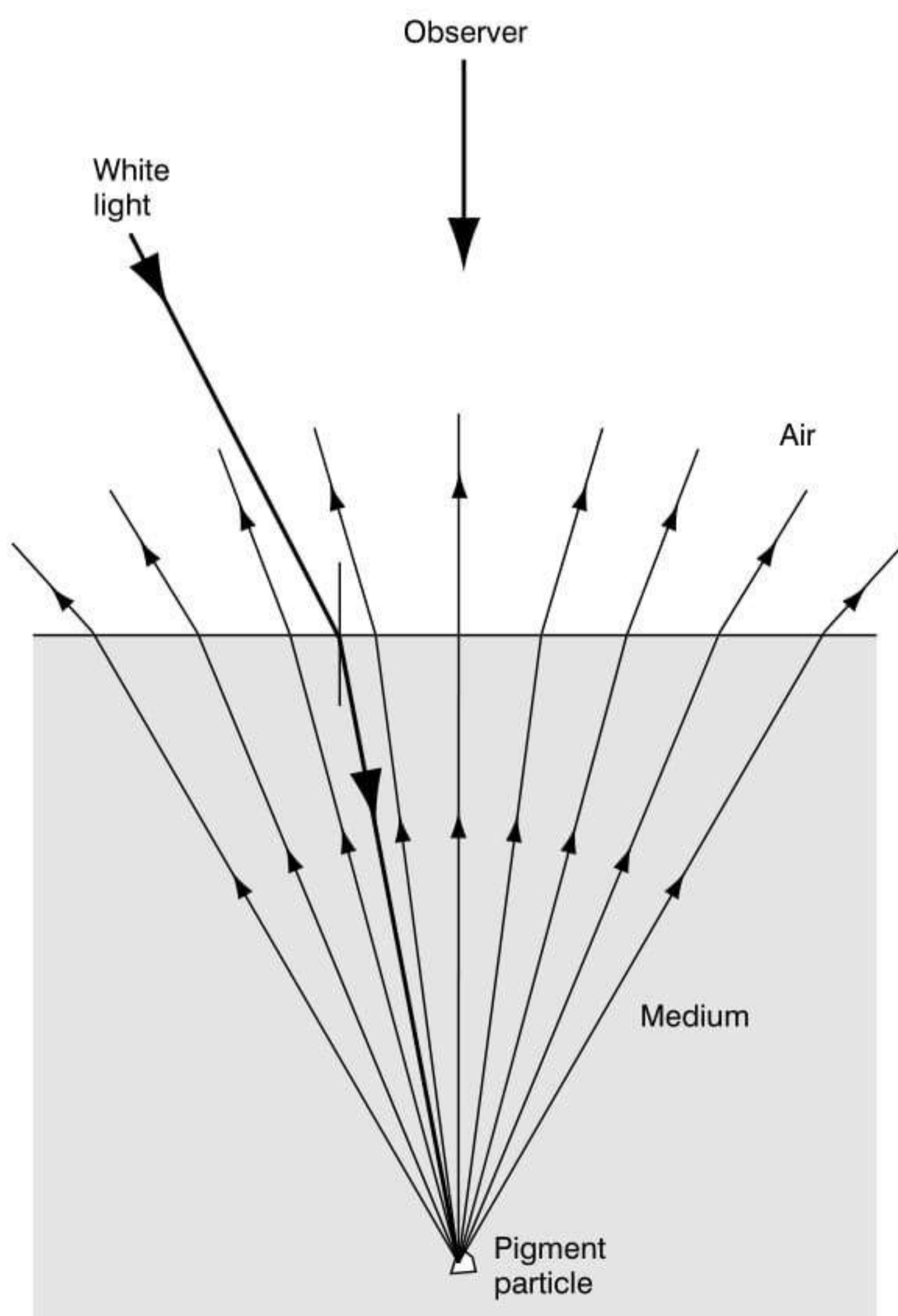


Figure 2.3 Scattering of light produced by a single very small pigment particle

- (c) have a refractive index greater than 1.5, this being that of the media in which white pigments are generally used.

In practical applications of pigments there will usually be white pigment to confer opacity and one or more coloured pigments to provide the colour. The main effects in this case are indicated in Figure 2.4, which shows the combination of a coloured pigment particle of a size considerably greater than the wavelength of light and a white pigment particle considerably smaller than that wavelength. If the coloured particle is also smaller than this, its colouring power is lost and its effect virtually the same as that of the white pigment particle. In practice most pigment particles produce both scattering and absorption effects.

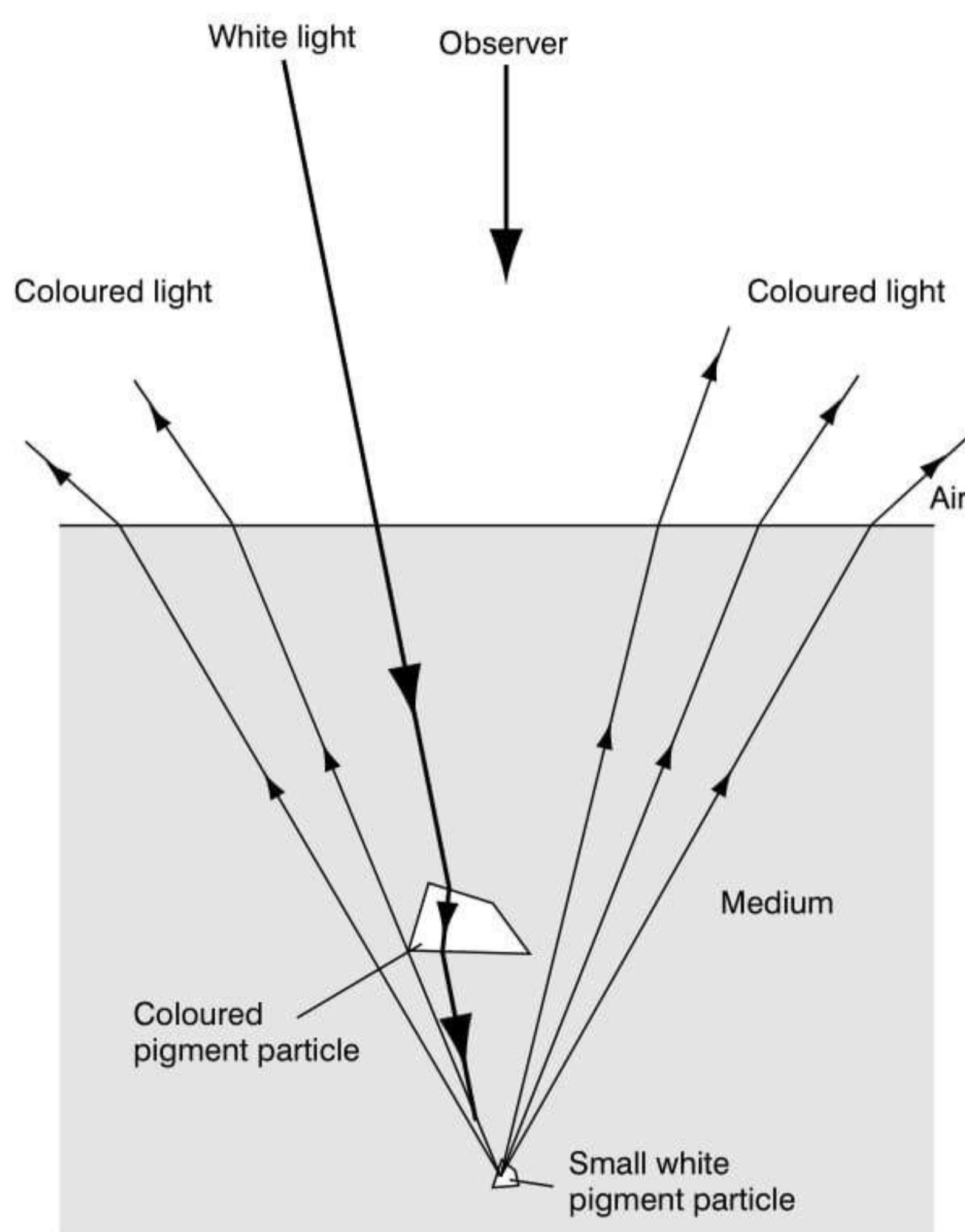


Figure 2.4 Combination of a coloured pigment particle and a very small white pigment particle

Even though this analysis takes account of both the predictions of geometric optics and of the wave theory of light, there are still further factors to consider. Every refraction is accompanied by some degree of reflection. Coefficients of light absorption depend on the plane of polarisation of the light with respect to crystal planes in the structure and pigments show both birefringence and dichroism, topics which are fully discussed in textbooks of physical optics.

In a concentrated dispersion of white and coloured pigments, each present in a range of particle sizes, a detailed analysis of ray directions becomes impossible. It is possible to deduce some general principles, however. These are that white pigments should be of a narrow size distribution, peaking in the region of 200 nm, and that coloured pigments should be of larger sizes, peaking around 500 nm, depending on the value of their absorption coefficients.

This analytical approach is difficult to apply to individual pigments because physical data relating to refractive index, dispersion curves and the absorption curves in the solid state are not available. A colligative approach, based on the Kubelka-Munk analysis which characterises pigments by only two constants, an absorption and a scattering coefficient, has been applied with considerable success to the computation of the proportions of pigments in mixtures needed to match a given colour. Much of the book *Colour physics for industry* is devoted to this topic [37].

There are also problems arising from the electrical interactions between different pigments and between pigments and the media in which they are dispersed, particularly when these are liquid paints and inks. This topic is discussed in the textbooks by Parfitt and Apps (amongst others), given in the bibliography at the end of this chapter.

2.12 SOLVENT DYES

Textile dyes can be dissolved or solubilised in water to a greater or lesser extent, this being essential for all conventional dyeing processes. Since solubility in water is generally accompanied by insolubility in nonpolar solvents, most textile dyes have this property. Solvent dyes, on the other hand, are soluble in organic solvents but insoluble in water. Solvent dyes are used as colour markers for the many different hydrocarbon fractions produced in oil refineries. Although the concentration of dye is low, the vast volumes involved makes the overall dye usage considerable.

Solvent dyes are also used for tinting transparent varnishes and lacquers in the furniture and leather industries, where the surface texture of the finished articles needs to be protected but not obscured. There is also a growing demand for coloured but transparent inks for printing on the ever-increasing amounts of plastic packaging of all kinds used for the food sold in supermarkets.

Solvent dyes are used to colour the transparent paints used to exploit the special properties of metallic pigments, as mentioned earlier. Another use for solvent dyes is in the colouring of many plastic articles to supplement the colouring power of pigments, if the use of pigments alone in a particular application is found to have undesirable effects on the physical properties of the plastic.

The new *Colour Index* volume *Pigments and Solvent Dyes* lists some 350 solvent dyes and gives their chemical structures, unlike earlier editions which named 800 dyes but included few structures. This fall in numbers is not because of any decreased use but rather the general contraction in numbers of all dyes used in the textile industry. Solvent dyes have been introduced not by attempts to synthesise new colorants but by selection and in some cases modification of known disperse dyes to meet the technical requirements. The majority of solvent dyes are azo compounds but among the blue dyes there are anthraquinones. The aqueous solubility of some of the parent sulphonated dyes has been reduced to acceptable levels by formation of their salts with heavy metals or long-chain alkylamines.

2.13 CONCLUSION

The diversity of chemical structures involved in pigment chemistry is much less than that of dyes, but extends from organic to inorganic compounds. The technology involved in the use of pigments in a wide range of different media is that of dispersing the pigment in the

medium, a process requiring quite different properties from those needed for dyes. As a result, even a compound that is chemically suitable for pigment use may not be acceptable in practice because it cannot be prepared in a physical form that allows its potential colouring properties to be exploited fully as a stable dispersion. This occurs quite frequently with the wide variety of plastic media now available and requiring to be coloured. Manufacturers of pigments meet these difficulties by selling the same pigment chemical in a series of different forms with additives and coatings chosen to suit the intended end-use.

This development has also been necessary because of the increased automation in many colour-using industries. For example, a computer colour match prediction recipe may call for the use of exact amounts of particular pigments and these have to be metered by volume into the machine that shapes the finished article. This simply cannot be done using dry powders, which were at one time the principal products of pigment makers. Dispersions of the component pigments with precise and constant colour strength are essential if large numbers of the finished articles are to be kept within acceptable colour tolerances.

The range of pigments commercially available is diminishing, though producers usually make several physical forms of the same pigment, each intended for specified applications. There are several reasons for the fall in numbers of different pigments. As well as the needs of the automated systems mentioned above, there has been a rationalisation of the range of intermediates available from the chemical industry, especially if an intermediate is no longer required for dye making. Certain pigments have been discontinued because they cannot meet the current demands from users for higher fastness standards, particularly to light. Low-volume production may be uneconomic when suitable substitutes are available.

The increasing use of instrumental colour match prediction, with the possibility, at least in theory, of matching wide colour ranges using only three or four pigments, as already achieved in colour printing, is yet another factor contributing to contraction of the pigment range. No doubt technical limitations such as dispersion stability will prevent such a drastic change happening in practice.

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The most extensive compilation of information about pigments is in the volume *Pigments and Solvent Dyes* (1997), which is part of the *Colour Index*. For various reasons, there is now less technical information about the chemistry of the synthesis and manufacturing methods for pigments than appeared in the 1982 volume, although much of this was in references to patents.