CHEMICAL SOCIETY REVIEWS

Some aspects of organic pigments

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Organic pigments are traditionally used in the mass colouration of plastics and synthetic fibres, and in surface coatings such as paints and inks. More recently, they have also found increasing use in a number of high technology industries. Commercial pigments must satisfy many performance criteria, which in turn are determined by their molecular, solid state and particle surface characteristics. This review highlights some of the important aspects of organic pigments which are of importance to both producers and users.

1 Introduction

Colour is an important and ubiquitous part of our everyday life and ever since pre-historic times, colours, be they inorganic or organic, have had profound anthropological, psychological, aesthetic, functional and economic impact on society.

During the past 140 years, since the discovery of mauveine by W. H. Perkin, there has been a remarkable development of the synthetic colourant industries.

Colourants are either dyes or pigments. To the colour chemist, it is important to distinguish between these two terms. Organic dyes are soluble substances mostly applied to various substrates from solution. A general characteristic of dyestuffs is their ability to provide colour in monomolecular disperse form solely by selective absorption of visible light. Organic pigments, on the other hand, are finely divided, coloured particulate solids which are practically insoluble in most solvents and in the media in which they are incorporated by adequate dispersion techniques. Organic pigments impart colour by selective absorption and/or scattering of visible light.

In the course of the last few decades, organic pigments have experienced rapid growth to become an industry of significant commercial potential. The traditional function of organic pigments has been to impart colour, and this will remain the major volume use of pigments for many years to come. Coloured organic pigments today are used in many industrial and consumer sectors to satisfy aesthetic needs, to communicate, identify, differentiate, or to secure and protect.

The aesthetic significance of coloured organic pigments extends from art, fashion to decoration, and more. Their use in cosmetics and mass coloured synthetic fibres is widespread in the fashion world. Decorative uses of organic pigments is abundantly manifest in the vehicle and machine industry, architecture and building, furniture and household, and leisure industries *etc.*, where pigmented paints, coatings and plastics find frequent application.

The most widespread use of coloured organic pigments is in the form of printing inks, followed by paints and plastics. The coloured packages, posters, and other diverse products from the printing ink industry are glaring examples of their use in communicating specific messages to the consumer.

When thinking of coloured organic pigments for identification, examples such as, company car fleets, red fire service cars, product brand colours, *etc.* come to mind. Organic pigments are used to print postage stamps and currency notes, facilitating their identification and differentiation. Using different coloured organic pigments to identify and differentiate cable coating, gas conduits, electric switches, yellow school buses *etc.* also has an implied safety aspect.

In recent times, however, organic pigments are finding increased use in a number of high technology industries, such as photo-reprographics, opto-electronic displays and optical data storage. In some of these applications, the pigment is still employed because of its colour imparting capability, while in other cases it performs a special function which is not based on its colour.

Organic pigments are commonly supplied in a number of different commercial forms including powders or granules (either surface treated or untreated), aqueous press cakes, pre-dispersed aqueous pastes, flushed pigments (dispersions in

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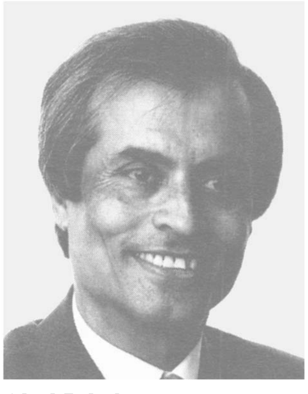

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viscous, aliphatic hydrocarbon-based media), resin pre-dispersed pigments, and plastic colour concentrates or masterbatches.

The commercial performance of a pigment in a vehicle system is defined by a long list of its application properties, such as its colouristic performance, rheological behaviour, durability and ecological compatibility/acceptability. From the end-user's point of view, the pigments must fulfil certain requirements with regard to such properties. However, in this article we shall restrict our discussions only to such characteristics as hue, tinctorial strength, transparency/opacity, resistance to heat, light, weather and solvent, and rheology and dispersibility.

The physical and chemical characteristics that control and define the performance of an organic pigment include its molecular, solid state and particle surface characteristics. Table 1 summarises the more important molecular and solid state parameters which primarily influence the end-use properties of the organic pigment.

The pigment manufacturers must design their products, accordingly, by judicious choice of the chemistry and solid state pigment elaboration techniques, to meet these performance requirements. This review article purports to highlight some of the above mentioned important aspects of organic pigments, without the intention of being exhaustive in its coverage.

2 Commercial performance criteria of organic pigments

The most fundamental performance criterion of a commercial organic pigment is its colour as manifested by its reflectance spectrum, which is most strongly influenced by the molecular absorption spectrum. Commercially, the most desirable property is probably the value in use, or the colour value per kg of the pigment. Colour value generally translates into tinctorial strength and purity of shade, both of which are dependent on the absorption spectrum intrinsic to the pigment structure, high molecular extinction coefficients and absorption spectra with sharp cut-offs representing the ideal profile.

Opacity or hiding power of a pigment is a function of its absorption coefficients, the absorption wavelength of light, its particle size, or light scattering coefficient and relative refractive indices of pigment and vehicle (pigment density). Light scattering has a powerful influence on opacity. As a rule of thumb, scattering and opacity are maximum when the pigment particle size equals half the absorption wavelength of absorbed visible light. As indicated in Table 1, colour strength and opacity can thus be best manipulated by controlling the chemical structure, crystal lattice parameters (*e.g.* modification) and particle morphology (*e.g.* size) of the pigment.

Table 1 Pigment performance and molecular/solid state parameters relationship

Commercial performance criteria		Molecular and solid state parameters
Colouristics:	hue/purity of shade	Molecular structure (λ_{max}), crystal lattice properties
	Colour strength	Molecular structure (ε_{max}), particle morphology
	Hiding power	Molecular structure (λ_{max}), particle morphology
Fastness:	Photochemical stability	Molecular structure, particle morphology and crystal lattice properties
	Heat stability	Molecular structure, particle morphology and crystal lattice properties
	Solvent fastness	Molecular structure, particle morphology
Rheology		Particle morphology, particle surface characteristics
Dispersibility		Particle morphology, particle surface characteristics

The fastness of a coloured organic pigment is a measure of its inherent ability to resist the chemical and physical influences to which it is exposed during and after its incorporation into a pigmented system. The most important fastness property of a pigment is its light and weather fastness, as measured by the extent of fading or darkening of a pigment colouration as a function of the duration of exposure to specified light and weathering conditions. The light fastness of an organic pigment is a function of the intrinsic molecular structure, as well as of the solid state properties of the pigment.

Heat stability is primarily a function of the pigment crystal lattice energy, as determined by the electronic, atomic and molecular interactions prevalent in the lattice. Under the drastic processing conditions for most plastics, a good organic pigment must feature sufficiently high heat stability, so as not to suffer any consequential change of shade through chemical degradation, change of crystal modification, or change in particle morphology as a result of Ostwald ripening or re-crystallisation of the pigment particles.

Poor solvent fastness of an organic pigment is a function of its solubility in the application medium and is manifested by its increased tendency to bleed or migrate from one pigmented substrate to another, or to migrate from within a pigmented medium to redeposit itself at its surface, or to re-crystallise to larger particles in a pigment dispersion medium. Solubility is an intrinsic molecular property.

3 Chemical features of organic pigments

The building blocks in organic pigments are molecules that determine, directly or indirectly, important performance properties of the pigments. Such organic pigment molecules are generally characterised by planar conjugated chromophoric systems featuring functional groups such as the $C{=}O$ and NH groups. In certain cases they may contain acidic and basic functional groups allowing precipitation of soluble dyes *via* salt and metal complex formation.

Organic pigments are classified according to their generic name and chemical constitution. Details of the chemical constitution of organic pigments is given in the Colour Index (C.I.) published by the Society of Dyers and Colourist.[1] Each chemical type is characterised by a C.I. number, for example, copper phthalocyanine (see Fig. 1) is designated C.I. Pigment Blue 15 ('C.I. Pigment' generally being omitted for brevity, and P.B., P.G., P.O., P.R., P.V. and P.Y. *etc.* used to designate blue, green, orange, red, violet and yellow pigments, respectively).

The development of organic pigments for colouration was triggered off by two landmark events in the history of colour chemistry, namely, the discovery of the first aniline dye, mauveine or aniline purple, in 1856 by the 18 year old William Perkin, followed by the discovery of the diazotisation reaction of aromatic amines by Peter Griess a few years later.

The first organic pigments to be released on the market at the turn of the century were all pure azo compounds with β-naphthol derivatives as coupling component (*e.g.* P.R. 1-3, P.O.5). Such products, along with the analogously structured laked azo pigments like P.R. 53:1 and P.R. 57:1, which are obtained by precipitation of the adequately functionalised azo dyes *via* salt formation, indeed mark the actual beginning of the era of organic pigments colouration. Replacement of the naphthol based coupling component by acetarylamide led to the first yellow azo pigments (Hansa Yellows, *e.g.* P.Y. 1). The azo pigments held sway over the organic pigment industry for several years until the advent of copper phthalocyanines in 1935. Many new organic structures, mainly featuring heterocyclic chromophores, have since been discovered and introduced as commercial organic pigments.

In terms of chromophore structures, roughly half the world market volume of synthetic organic pigments is comprised of pigments based on the azo chromophore, while a quarter of the volume is claimed by metal (mainly copper) phthalocyanines.

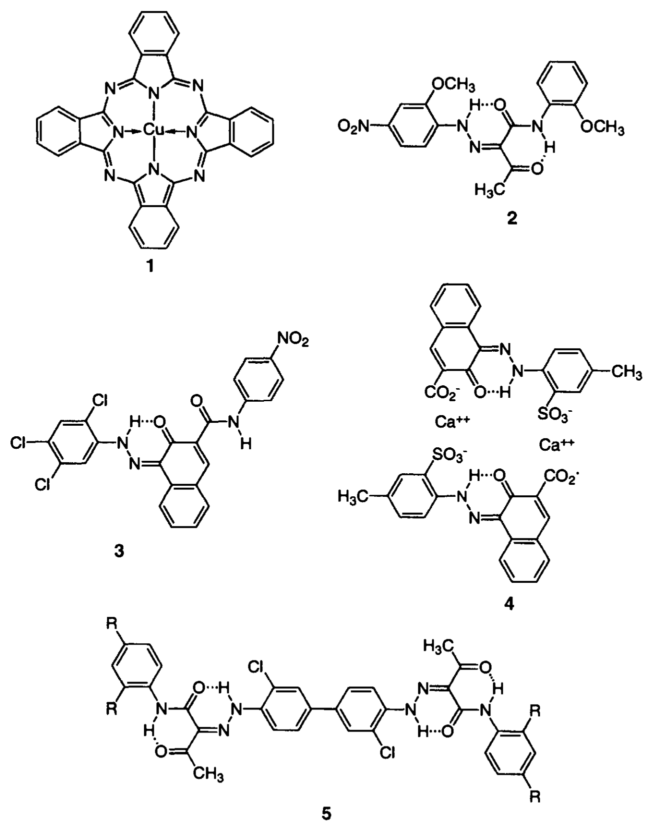


Fig. 1 Structures of some typical classical pigments. **1** C.I. Pigment Blue 15; **2** C.I. Pigment Yellow 74; **3** C.I. Pigment Red 112; **4** C.I. Pigment Red 57:1; **5** C.I. Pigment Yellow 13 (R = CH_3) and C.I. Pigment Yellow 12 (R = H).

The remaining 25% are primarily shared by a number of heterocyclic pigments, a few quinoid and indigoid structures and multidentate metal complexes, not taking into consideration the lakes of heteropoly acids with basic dyes.

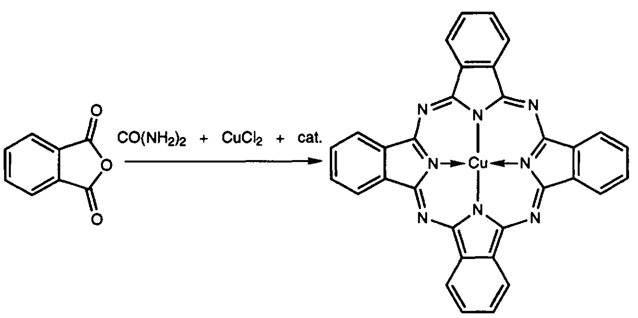
For a more comprehensive list of organic pigments and their constitution, the reader is referred to the recent publications by Herbst and Hunger,[2] Zollinger,[3] McKay *et al.*,[4] Iqbal *et al.*[5] and Jaffe.[6]

In the light of the diversity of chemical structure coupled with differing technical performance levels, it has become conventional to classify organic pigments into so-called classical pigments on the one hand and high performance pigments on the other.

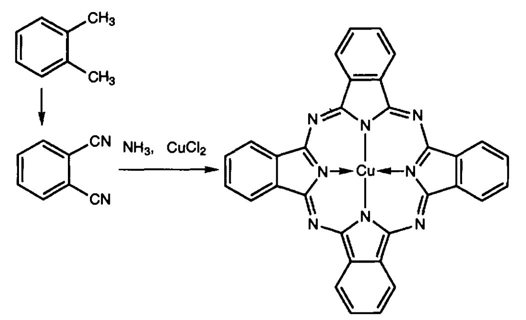
As implied by their name, classical organic pigments have been known for many decades. A few examples of their structure are given in Fig. 1.

The so-called azo pigments tend to exist as the hydrazone tautomer (as depicted in Fig. 1), stabilised by intramolecular hydrogen bonding.[7–9] Such monoazo and disazo pigments are relatively cheap and their technical performance level is not very high. However, copper phthalocyanines, which are also classified under classical pigments, are an exception to the rule, in as much as they have excellent all-round fastness properties.

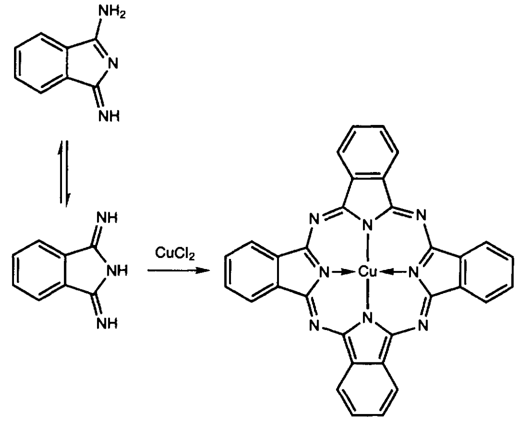
Copper phthalocyanine pigments are manufactured either from phthalic anhydride, urea, cupric chloride and ammonium molybdate (as catalyst) according to the following general Scheme 1,[2] or from phthalonitrile, obtained from ammoxidation of *o*-xylene and an appropriate cupric salt leading to the crude pigment[3] as shown in Scheme 2. A useful synthetic equivalent of phthalonitrile in copper phthalocyanine synthesis is 1,3-diiminoisoindoline or its tautomer 1-amino-3-imino-isoindolenine (Scheme 3).[3]



Scheme 1



Scheme 2



Scheme 3

The visible absorption spectrum of copper phthalocyanine is mainly determined by the tetraazaporphyrin chromophore structure and is little influenced by the four benzo rings, as was demonstrated by the fact that the spectrum did not change appreciably upon replacement of the benzo by naphtho or pyridine rings.[3] The only effective way of implementing a significant change in hue of copper phthalocyanine is by multiple substitution of hydrogen atoms at the benzo rings, for example, by chlorine and/or bromine to yield green pigments (P.G. 7 and 36).

Although several classical yellow and red monoazo and disazo red pigments may be used to colour paints and plastics, the majority of them are employed in printing inks manufacture. Disazo pigments like P.Y. 12 and 13, lakes of sulfonated monoazos like P.R. 53:1 and 57:1, and β copper phthalocyanine (P.B. 15:3) constitute the most important pigments for this purpose.

In comparison with classical organic pigments, high performance organic pigments tend to be of more recent origin and feature excellent all-round fastness properties. They are more costly to manufacture and find use in specialised and more demanding applications, such as in automotive paints and construction plastics, where exceptional light, weather, and heat fastness are required. Structural examples of high performance organic pigments are shown in Fig. 2.

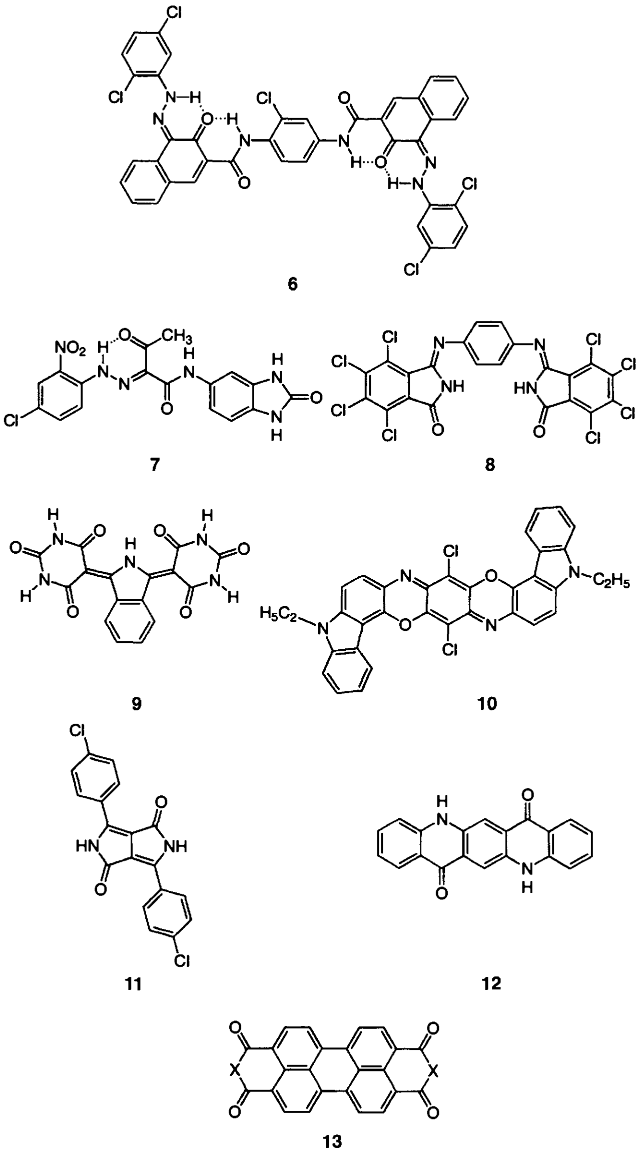


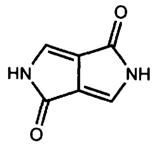
Fig. 2 Structures of some high performance organic pigments. **6** C.I. Pigment Red 144; **7** C.I. Pigment Orange 36; **8** C.I. Pigment Yellow 110; **9** C.I. Pigment Yellow 139; **10** C.I. Pigment Violet 23; **11** C.I. Pigment Red 254; **12** C.I. Pigment Violet 19; **13** C.I. Pigment Red 179 (X = NCH_3), C.I. Pigment Red 224 (X = O).

The two most significant chemical classes of high performance pigments are azo and polycyclic/heterocyclic pigments. Of the azo pigments, the most important ones include yellow to red disazo condensation products (*e.g.*, P.R. 144), yellow azo metal salts (*e.g.*, P.Y. 183), and yellow to red pigments based on benzimidazolone (P.O. 36).

A number of commercially important azomethine type pigments also belong to the high performance pigments; typical examples are isoindolinones (*e.g.*, P.Y. 110) and isoindolines (*e.g.*, P.Y. 139). In addition, two other types deserve mention, namely the anthraquinoids (*e.g.*, P.R. 177, P.B. 60) and dioxazines (*e.g.*, P.V. 23).

By far the most important heterocyclic pigments in the family of high performance pigments are quinacridones, including its various polymorphic forms (*e.g.*, P.V. 19), perylenes (*e.g.*, P.R. 179, 224), and the more recently commercialised diketopyrrolopyrroles (*e.g.*, P.R. 254). Of these, the diketopyrrolopyrrole pigments will be described in greater detail below.

The most recent addition to the class of high performance pigments are the 1,4-diketo-3,6-diarylpyrrolo[3,4-*c*]pyrroles, also known as 3,6-diaryl-2,5-dihydro-pyrrolo[4,3-*c*]pyrrole-1,4-diones. The underlying 1,4-diketopyrrolo[3,4-*c*]pyrrole (DPP) chromophoric system in these pigments combine the elements of indigo-like cross-conjugated vinylogous amidic and vinylogous hydrazine units in a rigid planar structural frame, essentially representing the lactam analogue of the 8π-electron fused ring hydrocarbon pentalene.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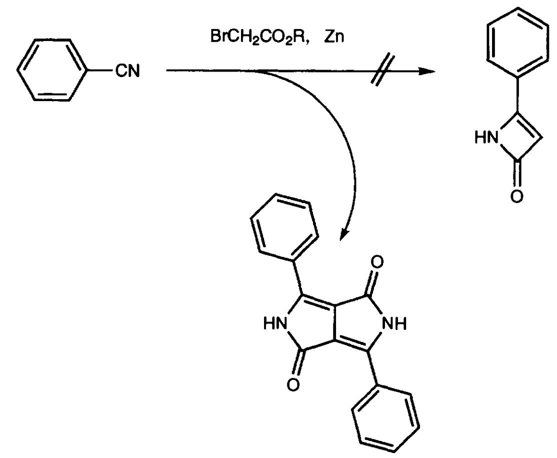
DPP: 1,4-diketopyrrolo[3,4-*c*]pyrrole

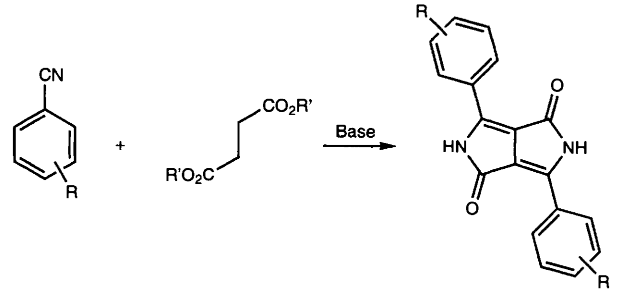
The first synthesis of a compound incorporating the DPP chromophore unit was reported in 1974 by Farnum, *et al.*,[10] who while attempting to synthesise 2-azetinones according to Scheme 4 quite inadvertently isolated a small quantity of the diphenyl DPP derivative (**15**) as a by-product, instead of the target β-lactam. A few years later, reconsideration of structural analogies of the DPP chromophore with several commercially well-known pigments triggered off reinvestigation of the chemistry and solid state properties of this class of compounds at Ciba-Geigy Company.[11] The investigations at Ciba culminated in the establishment of the pigmentary potential of the DPP class of compounds.



Scheme 4

A broad spectrum of brilliant shades, ranging from orange–yellow *via* blue–red to violet could be accomplished by simply exchanging the substituents at the *p*- and *m*-positions of the two phenyl rings attached to the DPP chromophore unit. Furthermore, selected members of this family of pigments offered outstanding light and weather fastness. Despite their low molecular masses, the diaryl DPP pigments are highly insoluble and remarkably resistant to chemicals and heat.[11] Such behaviour may be attributed, above all, to the presence of strong intermolecular bonding forces (*e.g.*, H-bonding, van der Waal's contact, π–π interactions between molecular planes) in the pigment crystal lattice, as was also corroborated by single crystal X-ray structure analyses of individual members of this group of compounds.

Unfortunately, however, the Reformatsky synthesis of DPP, as reported by Farnum[10] gave yields too poor to warrant commercialisation of the process. Keeping in mind the commercially important criteria of availability of starting materials, minimum number of synthetic steps, and technologically and ecologically feasible chemistry, the continued search at Ciba for alternative approaches to the DPP system ultimately led to the discovery of the elegant synthesis shown in Scheme 5, which could be tuned by appropriate choice of reactants and conditions to provide optimum product yield, consistent with good process economics.[12]



Scheme 5

Subsequent mechanistic investigations of the process opened an attractive preparative route of access to asymmetrically substituted aryl/alkyl and diaryl DPP derivatives.[13,14] Gompper *et al.*[15] have subsequently disclosed yet another route to diaryl DPP derivatives, comprising the reaction of succinamide with *N*,*N*-dimethylbenzamide diethyl acetal.

A qualitative inspection of the diaryl DPP molecule (Fig. 3) reveals several centres of reactivity in the molecule.

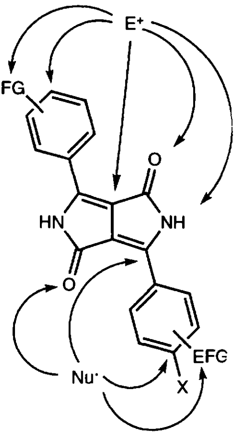
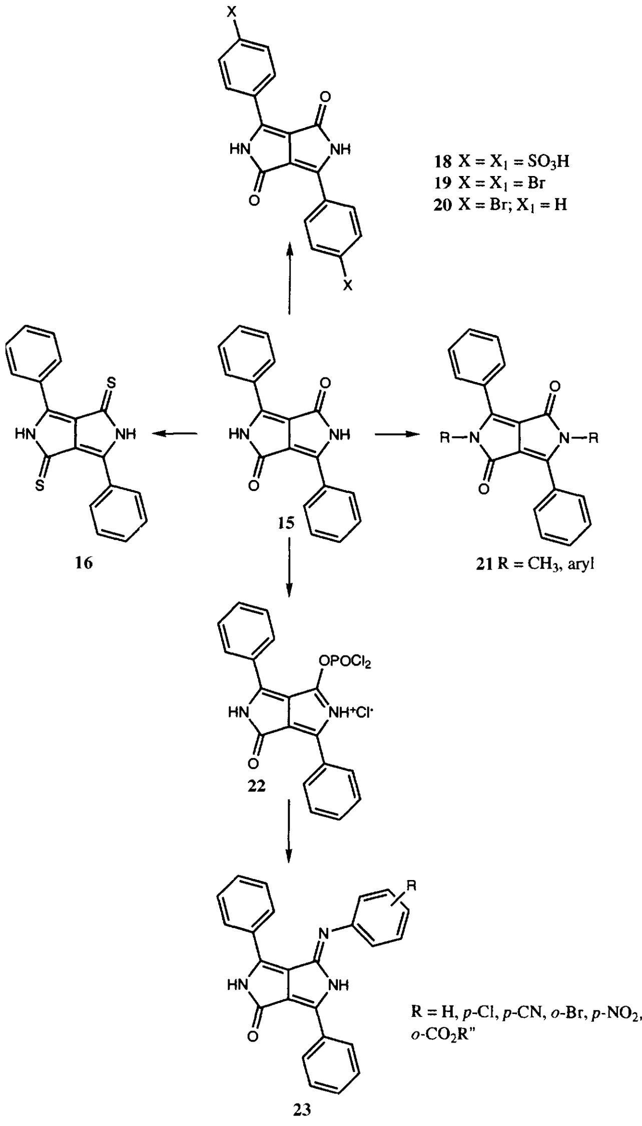


Fig. 3 Centres of potential chemical reactivity in the molecule of DPP

While the appropriately substituted phenyl rings should be capable of undergoing diverse electrophilic and nucleophilic substitution reactions, the bicyclic lactam chromophore unit incorporates three different functional groups, namely double bonds, carbonyl and NH moieties, each of them being potentially amenable to chemical transformation. In the interest of keeping the DPP chromophore intact, synthetic efforts have focused mainly on electrophilic aromatic substitution, *N*-substitution and nucleophilic transformations of the carbonyl group without incurring concomitant rupture of the heterocyclic nucleus.

Scheme 6 summarises a selection of products that can be obtained by direct chemical transformation of diphenyl DPP.

Currently, the most important member of the DPP class of pigments is Pigment Red 254 which is a very opaque yellow–red pigment of outstanding outdoor durability, brightness, and resistance to heat and chemicals. Another is the diphenyl DPP (P.R. 255), which is a high performance orange–red pigment. Both are used in automotive finishes, while a higher strength version of P.R. 254 is available for pigmentation of plastics.



Scheme 6

4 Solid state properties of organic pigments

Unlike dyes, which are present in polymeric substrates as either single molecules or small clusters, pigments are applied in the form of discrete crystalline particles well dispersed in the medium. Their overall pigmentary performance therefore cannot be adequately described in terms of the properties of the individual molecules. The colouristic and fastness properties of a pigment, as well as some other application properties, are significantly influenced by its solid state characteristics. The most important solid state parameters include crystal modification, crystallinity, particle size, shape and state of aggregation. In addition, the formation of pigment solid solutions and mixed crystals can also bring about unexpected effects.

4.1 Crystal formation and growth

By virtue of their structural features, pigment molecules exhibit a strong tendency to form highly ordered crystalline assemblies. The main driving forces for such crystal formation are intermolecular hydrogen bonding, π–π stacking between adjacent planar molecules and van der Waal's interactions. The overall effect of such interactions is generally believed to lead to stabilisation of the crystal lattice through lowering of energy. The tendency of crystal formation and growth can be seen clearly when a layer of copper phthalocyanine, obtained *via* vapour deposition, is subjected to a solvent treatment. When the

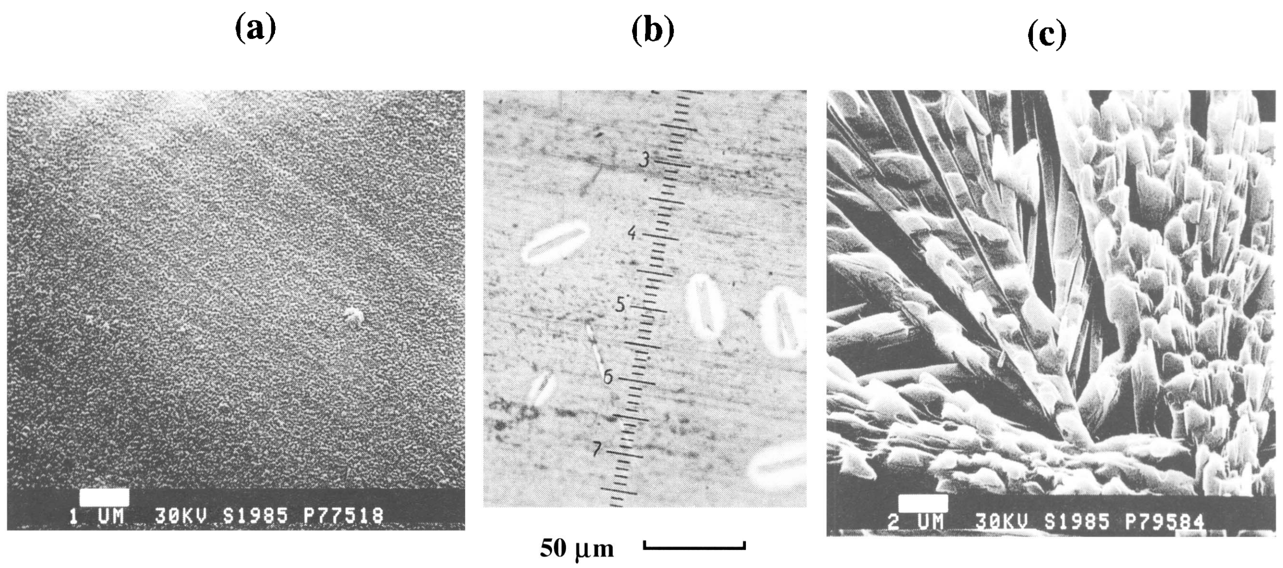


Fig. 4 (*a*) Scanning electron micrograph of a CuPc layer (0.15 µm) before solvent treatment; (*b*) optical micrograph of the same layer after one week of xylene vapour treatment, (*c*) scanning electron micrograph of the layer after four weeks of exposure to xylene vapour

partially amorphous pigment layer [Fig. 4(*a*)] is exposed to xylene vapour at room temperature for one week, long needle-shaped crystals are formed as shown in Fig. 4(*b*). Prolonged xylene vapour exposure eventually converts the entire layer of the less stable α-form into the more stable, highly crystalline β-form [Fig. 4(*c*)].

In many cases, the absorption spectrum of an organic pigment undergoes a change upon transition from the molecular to the crystalline state. This is illustrated in the case of a DPP pigment.[16] In solution, diphenyl DPP shows a green–yellow fluorescent colour, whereas in the solid state it is bright red. In Fig. 5 the absorption spectra of both states are plotted together, showing a bathochromic displacement of the maximum absorption of *ca.* 40 nm from the solution spectrum to the solid state spectrum. The colour shift can be attributed to intermolecular hydrogen bonding in the solid state.

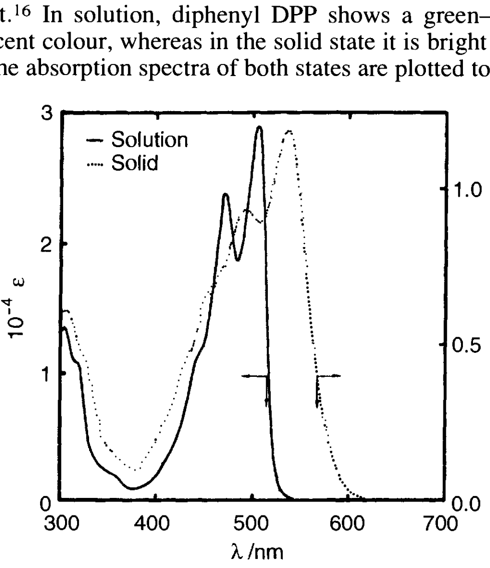


Fig. 5 Solution spectrum of DPP in DMSO (solid line) and solid state spectrum of the DPP thin film obtained *via* vapour deposition (dotted line) (Reproduced by permission from Mizuguchi and Wooden.[16])

4.2 Polymorphism

A large number of pigments are known to be polymorphic, in other words, there are different ways in which molecules with the same chemical constitution may be arranged within the crystal lattice, resulting in differently structured crystals, commonly denoted as crystal modifications or polymorphs. Each of the polymorphs has its own characteristic lattice energy and hence its stability. The readiness with which a pigment is converted from one modification into another depends upon the energy barriers between such modifications. To be of value, polymorphs should offer useful and distinct property profiles and sufficient stability to avoid unwanted phase transitions. Sometimes an unstable modification, if commercially attractive, can be stabilised by appropriate chemical and physicochemical treatment.

Crystal modifications are usually characterised by their distinctive powder X-ray diffraction patterns. Crystallographically polymorphs are classed as distinct substances. In general, X-ray diffraction patterns from different polymorphs bear no relationship to each other. Some pigment polymorphs are almost indistinguishable in appearance except X-ray diffraction pattern, whereas others differ so widely in their colouristics and other properties that at first glance they would not be considered even to be of the same chemical type.

As a typical example of polymorphism, copper phthalocyanine is known to occur in no less than five crystal modifications,[2] *i.e.*, the α-form (red-shade blue), the β-form (green-shade blue) and the γ-, δ- and ε-forms. The α-form *per se* (C.I. Pigment Blue 15) is not stable, it tends to revert to the β-form. Of commercial interest are the phase-stabilised α-form (C.I. Pigment Blue 15:1) and the β-form (C.I. Pigment Blue 15:3). The stabilisation of the α-form is achieved by partial chlorination, about 0.5 Cl per molecule being sufficient to prevent reversion to β-form. In Fig. 6, X-ray powder diffraction diagrams of the α- and β-forms of copper phthalocyanine are compared.

In the case of DPP pigments, recent studies carried out in our laboratories have led to the identification of a few new crystal modifications, *e.g.* the β-form[17] of C.I. Pigment Red 254. In paint colouration this β-form is significantly more yellowish as compared with the α-form, as is illustrated in Fig. 7.

4.3 Solid solutions and mixed crystals

Analogous to liquid solutions, in the solid state, if a binary (or multi-component) mixture is prepared by methods other than simple mechanical mixing, one of the components may assume the role of the solvent (host) while the other behaves as the solute (guest), thus forming a 'guest-host' solid solution. Molecules of the 'guest' compound enter the crystal lattice of the 'host' and, as a consequence, the X-ray powder diffraction pattern of such a solid solution is either the same as, or very similar to, that of one of the components, the 'host'. The term solid solution refers to a crystalline phase which exists over a

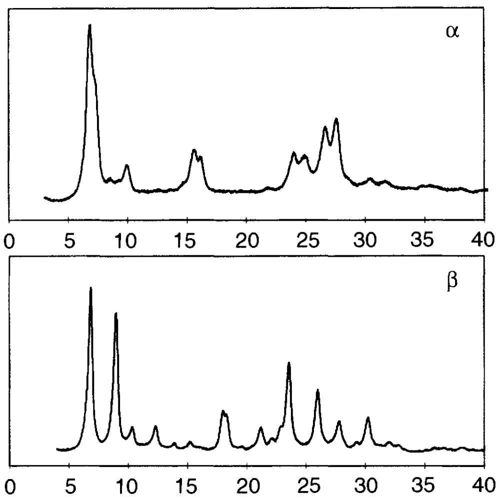


Fig. 6 X-ray powder diffraction patterns of copper phthalocyanine: the α-(upper) and the β-(lower) crystal modifications

range of compositions.[18] X-Ray diffraction patterns of solid solutions may undergo a progressive change in one or both of two ways as the composition varies. If the constituent molecules are not identical in size, then the unit cell size may alter which could result in an angular movement of the peaks. On the other hand, if the substituting molecule does not have the same X-ray scattering factor, the intensities of the diffraction peaks may alter. In certain cases a unique diffraction pattern, different from either of the component pigments, is obtained at a specific pigment composition. It is customary to denote such a product as a mixed crystal.[18,19] A dramatic change in performance, resulting from the synergistic effect, often accompanies the formation of such mixed crystals. A loose analogy can be drawn between a mixed crystal and an azeotrope in the liquid state.

In contrast to physical mixtures where an additive effect regarding colour and other properties is usually the case, a solid solution or a mixed crystal often shows non-additive, unpredictable colouristic and other performance properties. If crystallographically pure, a solid solution or a mixed crystal will behave just like a single pigment.

The phenomena of solid solutions and mixed crystals can be advantageously exploited in practice to extend an existing range of commercial pigments, by widening their colouristic scope and at the same time improving fastness and other application properties.

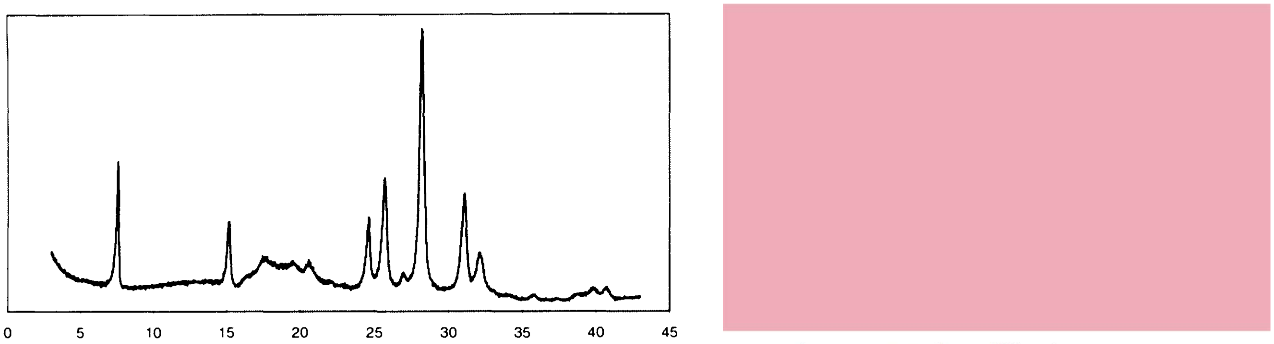
Examples of pigment solid solutions are available in the literature. Solid solutions among quinacridones, substituted and unsubstituted, for example, have been prepared with the colours ranging from orange, gold, red to maroon.[20,21] Improvement in pigmentary performance has also been noted. More recently, solid solutions involving acetoacetanilide, as well as diacetoacetanilide azo pigments have been reported.[9,22]

Investigations in our own laboratories have led to the recent discovery of DPP mixed crystals.[23] It is found that equimolar amounts of two different DPP pigments can combine and form an entirely new crystal lattice. The X-ray diffraction pattern of the resulting mixed crystal is different from either of the two constituent DPP pigments. This is exemplified by the mixed crystal of the unsubstituted DPP and the *tert*-butyl substituted DPP. A very significant bathochromic colour shift is seen concomitant to the formation of the mixed crystal. This is illustrated in Fig. 8.

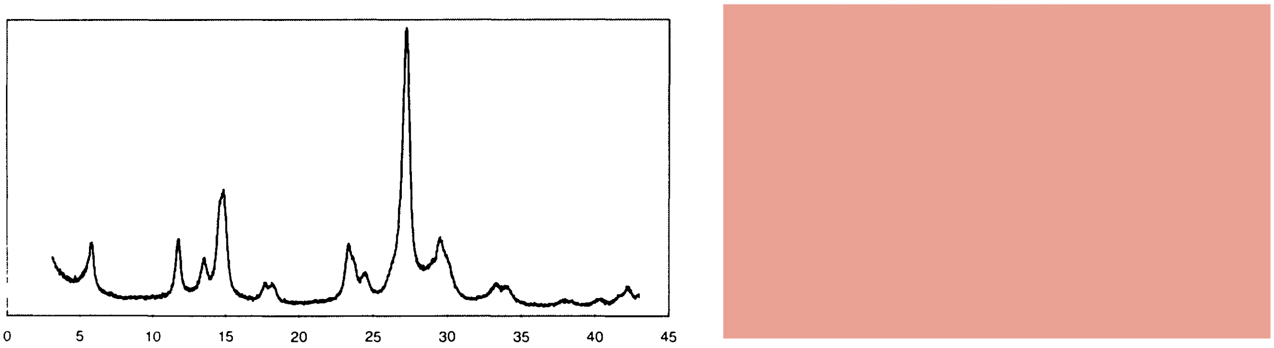
4.4 Isomorphism

Pigments of different chemical constitution but which are isostructural, *i.e.* those which have similar crystal cell dimensions and in which the molecules have similar positions with respect to each other, are called crystal isomorphs. It is obvious that if two pigments are isomorphs and if the X-ray scattering of the pigments is similar, this will give rise to very similar diffraction patterns.

Isomorphism is generally observed with pigments from the same chromophore class. Some isomorphs of monoazoacetanilide pigments have been reported,[24] the monobromo and dibromo analogues of C.I. Pigment Yellow 3 being good examples. C.I. Pigment Blues 15 and 15:1, mentioned earlier, are also isomorphs. More recently, a similar observation was



the α - crystal modification



the β - crystal modification

Fig. 7 C.I. Pigment Red 254, the α-(above) and the β-(below) crystal modifications in an alkyd resin system

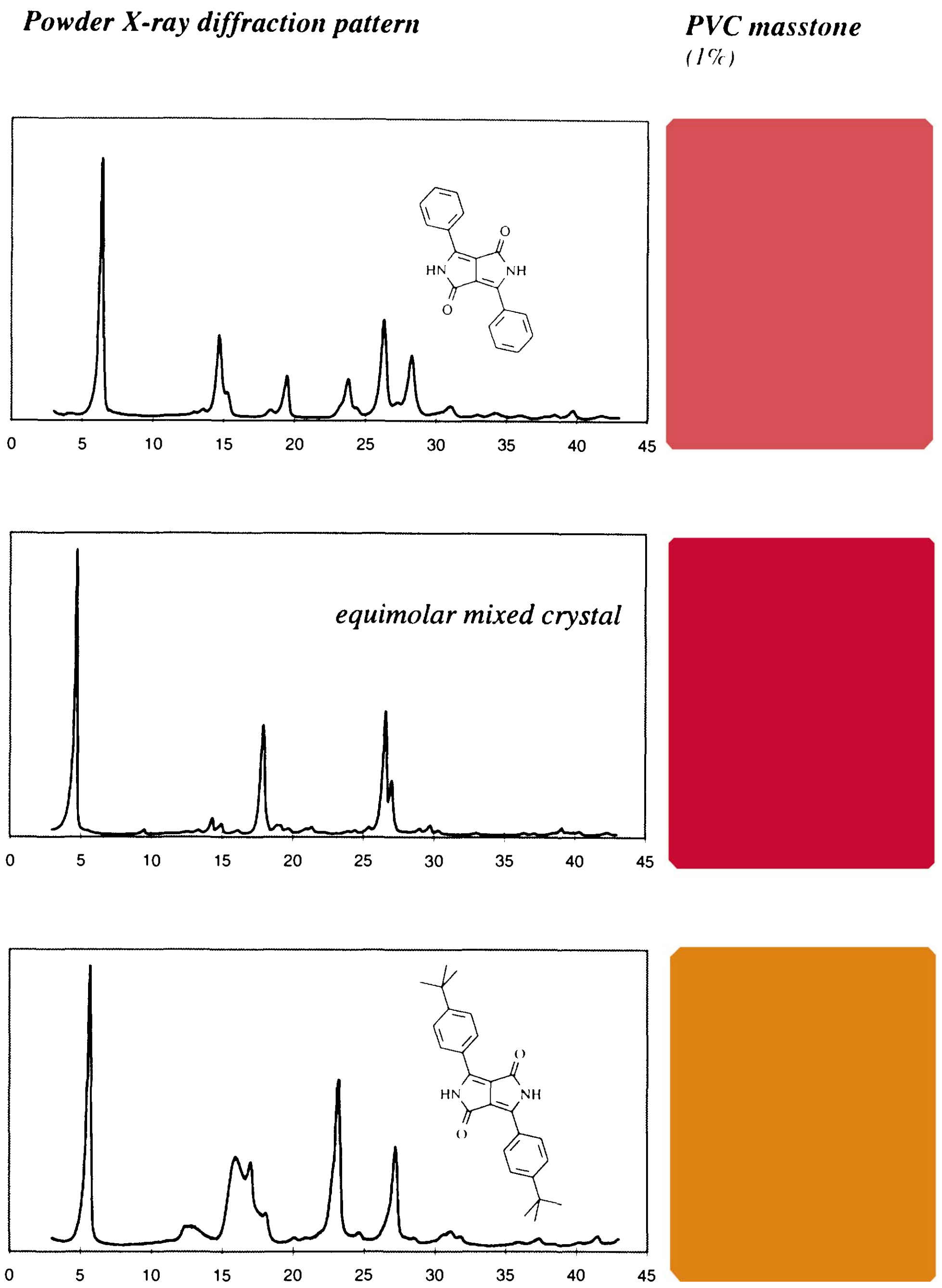


Fig. 8 PVC coloration and X-ray diffraction pattern of a binary DPP mixed crystal, as compared to the component DPP pigments

made in the disazo diarylide series of pigments for C.I. Pigment Yellow 14 and C.I. Pigment Yellow 63, the two pigments showing strikingly similar colouristic properties.[9]

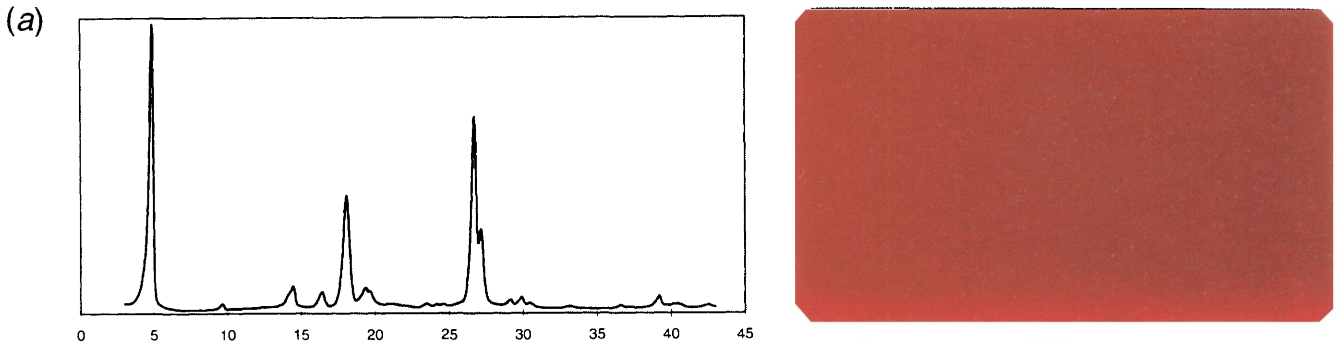
Another example is the crystallographic mimicry of asymmetric DPP pigments by equimolar binary mixed crystals of symmetric DPPs.[23] Thus the X-ray powder diffraction patterns of a mixed crystal, *e.g.* see above, and the corresponding asymmetric DPP were compared. They have been found to be nearly identical. From colouristic point of view, the two isomorphs are also identical. This is illustrated in Fig. 9.

4.5 Crystallinity

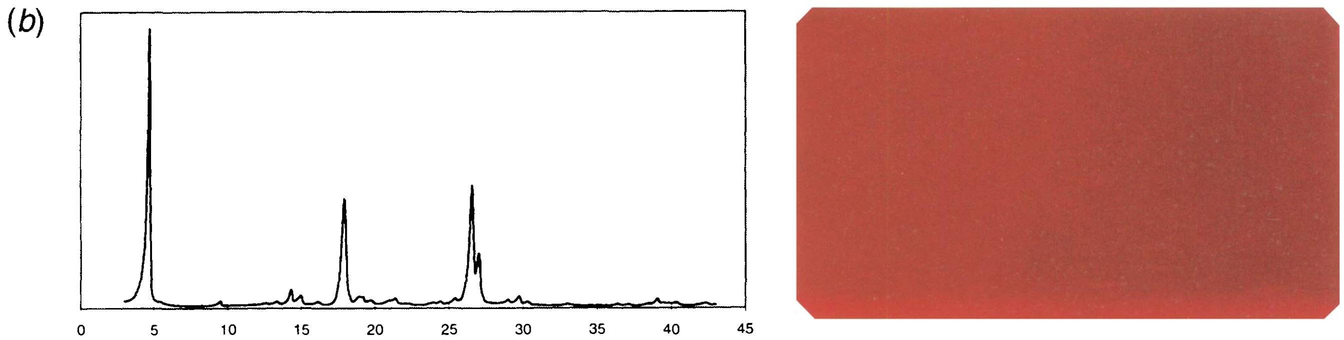
Immediately after their formation, either by grinding or by precipitation, organic pigments tend to show low crystallinity, with many internal and external defects. In practice, conditioning and finishing treatments are usually applied in order to remove or minimise the defects and hence to improve crystallinity. This leads, in general, to improved performance properties of the pigment. More crystalline pigments have lower lattice energy and therefore they show better fastness properties. Another characteristic of crystalline pigments is the lower susceptibility to aggregation, which makes them easier to disperse. In addition, crystallinity can also affect optical properties. For example, the absorption maximum and fluorescence of the untreated amorphous phase of C.I. Pigment Red 31 is shifted to longer wavelengths and the maximum extinction coefficient increased upon thermal conversion to the crystalline phase.[25]

4.6 Crystal size

The crystal size of a pigment has an important effect on the colour strength, opacity/transparency, photochemical and thermal stability and viscosity. Fig. 10 gives a qualitative correlation between particle size and some of the important parameters of a pigment dispersion.



the asymmetric DPP



the binary symmetric DPP mixed crystal

Fig. 9 Mimicry of an asymmetric DPP (*a*) by a binary DPP mixed crystal (*b*): PVC colouration and powder X-ray diffraction patterns

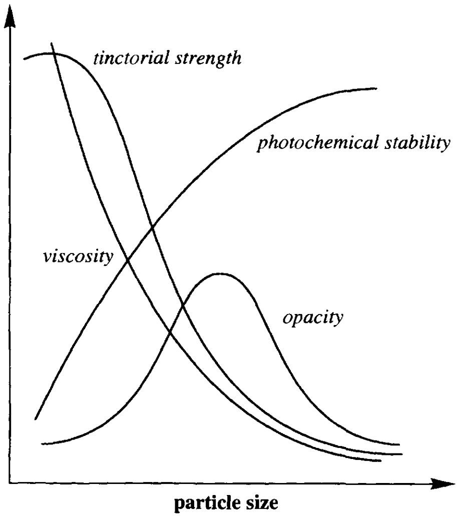


Fig. 10 Dependence of some pigment performance parameters on particle size

Colour strength increases, in general, as mean particle size decreases. This has been firmly established by theoretical elaborations,[26] experimental confirmation,[27] and practical usage. The highest dependence is found to occur at $\leqslant$ 0.1 μm.

The shade of a dispersion can be affected to a certain extent by a reduction of pigment particle size. An example of this is C.I. Pigment Yellow 34, which becomes greener as the size is reduced.[28]

Another important aspect is size distribution. In general, a wide particle size distribution results in lower colour strength and dullness or dirtiness in shade.

The opacity/transparency of a dispersion is affected by particle size and size distribution of the pigment. Thus, in a given medium, there is a maximum in opacity at mean particle size (0.2–0.5 μm).[29] Opacity at a given size is greater the narrower the size distribution.

Similarly, the transparency of a pigment-vehicle system is also dependent upon particle size. A high degree of transparency is an essential requirement of inks for the printing industry, and of paints for special effects (metallic, pearlescent, *etc.*). In such applications, pigments with very small particle sizes are used.

A demonstration of particle size effect on transparency/opacity of the pigment-vehicle system is provided by an experimental DPP pigment, which is prepared in two different sizes. The electron micrographs and PVC colouration over contrast paper are shown in Fig. 11. It is remarkable to note that equal amounts of the same pigment of variable particle size applied under same conditions give significantly different colour appearances.

5 Surface characteristics of organic pigments

The (physicochemical) nature of the particle surface of an organic pigment is to a large extent a function of its intrinsic molecular chemistry. Such surface properties, superimposed with crystal lattice properties (such as crystallinity, crystal modification) and particle morphology parameters (such as size and shape), ultimately account for the surface energy of pigment particles. Thus, in general, the more amorphous a particle the higher is its surface energy. Moreover, as the size of the primary pigment particles is reduced, a natural consequence is the rapidly increasing area of surface created, accompanied by a parallel increase of the total surface energy. These are active surfaces and have a tendency to react in any way which reduces the overall energy level. The small particles can therefore aggregate (stick to each other), or adsorb other chemical species such as solvent, surfactant or resin molecules from solution.

The phenomenon of aggregation can have multiple detrimental effects. First, it negatively influences the dispersibility and dispersion stability of the pigment. The effectiveness of organic pigments in imparting colour depends on how well they are dispersed in the application medium. Secondly, increased structure formation in dispersions leads to a reduction in the flow of such systems due to higher viscosity. Sometimes, the surface chemical character can also influence other mechanical properties of the application media, for example, distortion or warpage of moulded plastic articles.

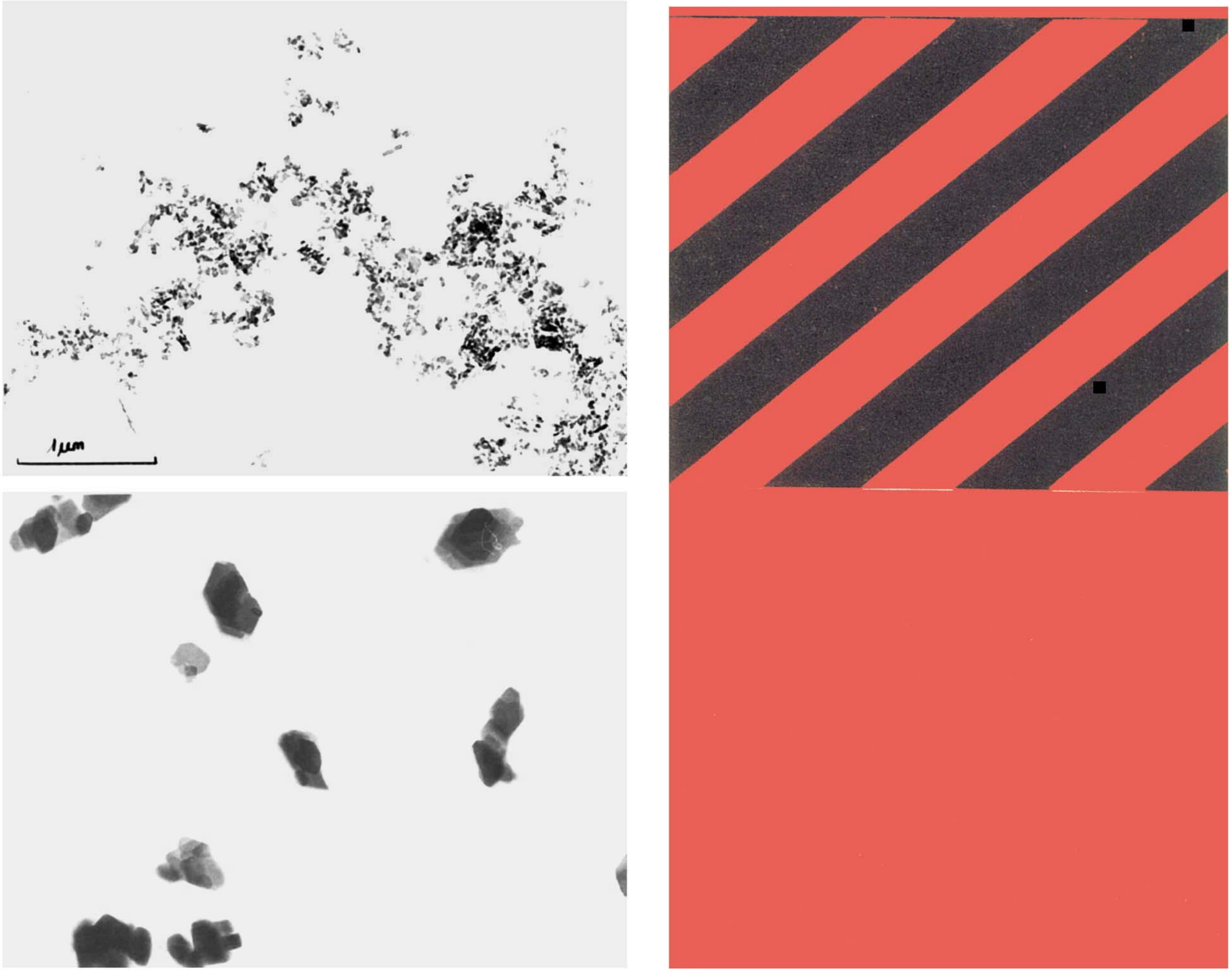


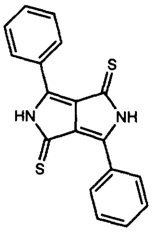
Fig. 11 Experimental DPP pigment samples of different particle sizes: PVC over contrast paper, together with the corresponding TEM photos

The most efficient way of controlling aggregation and its consequential effects is through effective modification of the interfacial properties by introduction of certain types of additives that adsorb to the pigment particle surfaces and anchor functional groups there. Several surface treatment procedures can be applied to improve the surface characteristics of an organic pigment. Most of them have in common the fact that they promote the formation of an adsorbed layer containing well-solvated, extended-chain molecules. The physicochemical mechanism involved is probably steric stabilisation, although electric charge stabilisation may play some part in aqueous dispersions. Details of these types of mechanism are given elsewhere.[30]

6 Some high-technology applications of organic pigments

Recently, pigments, as well as dyes, are becoming increasingly important in the electronics industry. In some applications, the role of the pigment is the conventional one of imparting colour, such as in colour filter pigments for liquid crystal displays and electrostatically charged toners and inks for non-impact printing technologies.[31] In many other applications, it is the special functional properties of the pigment, such as fluorescence, electro-luminescence, photo-conduction and selective absorption of infrared radiation, which are exploited. A novel erasable optical memory device has been recently claimed by Langhas, *et. al.*[32] which is based on the thermal transformation of a fluorescent into a non-fluorescent modification of a dimorphic DPP pigment. Electroluminescent elements containing a fluorescent DPP derivative in the luminescent layer have likewise been claimed.[33]

Information storage systems utilising solvent and NIR laser induced phase change of thio DPP derivative **(16)** as the recording medium, have been described.[34] The same thio DPP derivative also exhibits interesting photo-conductive properties, and its use as charge generating material in the preparation of organic photo-receptor drums for laser beam printers has been extensively investigated.[35] Recent claims have also been made on the use of diphenyl DPP and its phenyl ring-substituted derivatives as charge generating materials for plain paper copiers and laser printers.[36]



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thio DPP derivative

7 Summary and outlook

The conventional role of organic pigments has been to impart colour to a substrate. In recent years, organic pigments are finding increasing use in the high technology industries of electronics and opto-electronics. In both cases, the commercial success of a pigment is dependent on the fulfilment of a series of end-user demands, which define the technical performance properties of the product. To achieve the desired technical performance profile, the pigment manufacturers need to fine-tune the intrinsic molecular and solid state parameters of their product.

In retrospect, there has been a remarkable growth in the pigment industry over the past one hundred and forty years. Traditionally, the main driving forces behind such a development have been the demand for better technical performance in terms of colouristics and stability on the one hand, and economic considerations on the other. In more recent times, additional factors, such as ecological concern and the emergence of novel markets and engineering trends, have gained increasing importance and will continue to shape the future of the pigment industry. While such a development may pose several challenges to be mastered, it also creates new opportunities, lending vital impetus to the pigment industry. To meet these challenges, the pigment industry will need to create and develop innovative products, processes, and applications. At the same time, it will be indispensable to invest in longer term research in order to secure continued growth of the industry well into the next century.

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