1 General

1.1 Definition: Pigments and Dyes

Colourants are classified as either pigments or dyes. Pigments are inorganic or organic, coloured, white or black materials that are practically insoluble in the medium in which they are incorporated. Dyes, unlike pigments, do dissolve during their application and in the process lose their crystal or particulate structure. It is thus by physical characteristics rather than by chemical composition that pigments are differentiated from dyes [1]. In fact, both are frequently similar as far as the basic chemical composition goes, and one structural skeleton may function either as a dye or as a pigment.

In many cases the general chemical structure of dyes and pigments is the same. The necessary insolubility for pigments can be achieved by avoiding solubilizing groups in the molecule or by forming insoluble organic structures. Carboxylic and especially sulfonic acid functional groups lend themselves to the formation of insoluble metal salts (lakes); the formation of metal complex compounds without solubilizing groups and finally suitable substitution may decrease the solubility of the parent structure (e.g. carbonamide groups).

Pigments of many classes may be practically insoluble in one particular medium, yet dissolve to some extent in another. Partial solubility of the pigment is a function of the application medium and processing conditions, especially of the processing temperature. Important application properties of pigments and/or pigmented systems, such as tinctorial strength, migration, recrystallization, heat stability, lightfastness, and weatherability, are often determined by the portion of pigment that dissolves to a minor degree in the vehicle in which it is applied.

Monohydrazone yellow pigments of the Hansa Yellow type (e.g. Pigment Yellow (P.Y.) 1, P.Y.3; Section 2.3.4.2) may serve as an example. Their solubility in air-dried alkyd resin systems is so negligible that they are considered insoluble, which explains their frequent use in such media. Since their solubility increases with increasing temperature, they migrate considerably in vehicles such as various oven-dried varnish systems or in plastics. This results in bleeding or blooming (Section 1.6.3). Strong migratory tendencies preclude their use in such high temperature applications. Even slight temperature changes in the course of...
pigment incorporation into its application medium may often determine the commercial fate of a pigment. Moreover, the inherent tinctorial properties of a product in a particular vehicle system are sometimes compromised by difficulties such as recrystallization, which arises through a certain solubility of the pigment in its medium.

Under certain circumstances, it may even be advantageous to have a pigment dissolved to some degree in its binder system in order to improve certain application properties such as tinctorial strength and rheological behaviour. Such conditions arise when special amine-treated diarylide yellow pigments are incorporated in toluene-based publication gravure inks (Section 1.8.1.1). In toluene, up to 5% of the amine-treated pigment may be either dissolved or dispersed to a nearly molecular level. This improves the tinctorial strength and decreases the viscosity, which in turn enhances the rheology of the pigmented ink. The performance of a colourant in its role as a commercial pigment is therefore defined by its interaction with the application medium under the conditions that govern its application.

1.1.1 Organic and Inorganic Pigments

In some application areas, inorganic pigments are also used to an appreciable extent, frequently in combination with organic pigments. A comparison of the respective application properties of inorganic versus organic pigments shows some fundamentally important differences between the two families.

Most inorganic pigments are extremely weatherfast (Section 1.6.6) and many exhibit excellent hiding power (Section 1.6.1.6). Their rheology is usually an advantage (Section 1.6.8), being superior to that of most organic pigments under comparable conditions. In white reductions, however, many inorganic pigments have much less strength than organic pigments. With few exceptions such as Bismute Vanadate, Molybdate Red, Chrome Yellow, and cadmium-based pigments, inorganic pigments provide dull shades. Since there are only relatively few inorganic types, the spectral range that is accessible by inorganic pigments alone is very limited. Many hues cannot be produced in this manner.

Inorganic pigments not only exhibit colouristic limitations but also frequently present application problems. Ultramarine Blue, for instance, is not fast to acid, while Prussian Blue must not be exposed to alkalis. Such limitations preclude the application of, especially, Prussian Blue in paints that are to be applied to a basic substrate (e.g., exterior house paints). In the red range of the spectrum, iron oxide red pigments produce weak hues of comparatively little brilliance. Molybdate Reds and Chrome Yellows lend themselves to a host of applications but are nevertheless sensitive to acids and light. There are stabilized versions of such pigments that claim improved lightfastness and acid resistance. These products also claim to be chemically fast to hydrogen sulfide, which affects the brightness of a coating through sulfide formation. However, if the particle surfaces of such types are damaged during the dispersion process, the above-mentioned deficiencies are apparent at the damaged site.
Poor tinctorial strength and lack of brilliance restrict the use of inorganic pigments in printing inks. There are areas of application, however, where it is hardly, if at all, possible to replace the inorganic species by an organic pigment. The ceramics industry, for example, requires extreme heat stability, which precludes the use of organic compounds. Thus, the organic and inorganic classes of pigments are generally considered complementary rather than competitive.

1.2 Historical

The history of pigment application dates back to prehistoric cave paintings, which give evidence of the use of ochre, haematite, brown iron ore, and other mineral-based pigments more than 30,000 years ago. Cinnabar, azurite, malachite, and lapis lazuli have been traced back to the third millennium BC in China and Egypt. With Prussian Blue, in 1704 the first non-natural inorganic pigment was synthesized. It was not until a century later that Thenard produced his Cobalt Blue. Ever increasing expertise and technology led to the production of Chrome Yellow, Cadmium Yellow, several synthetic iron oxides covering parts of the ranges of yellow, red, and black hues, Chrome Oxide Green, and Ultramarine.

Important twentieth-century developments include the addition of Molybdate Red to the series of inorganic synthetic colouring matters in 1936; Titan Yellow followed in 1960.

Later newly developed inorganic pigments have been introduced to the market, such as bismuth–molybdenum–vanadium oxide pigments for lead-free formulation, or cerium sulfide pigments, which can be used as a replacement for cadmium sulfide pigments.

The beginning of organic pigment application dates to antiquity. It is certain that the art of using plant and animal ‘pigments’ to extend the spectral range of available inorganic colourants by a selection of more brilliant shades had been practised thousands of years ago. However, for solubility reasons, most of these organic colours would now be classified as dyes rather than pigments. Even in antiquity, they were used not only for dyeing textiles but also, due to their ability to adsorb on mineral-based substrate such as chalk and china clay, for solvent resistant coatings for decorative purposes. These materials later came to be known as lakes or toners. For thousands of years, derivatives of the flavone and anthraquinone series have been the major source of natural colours for such applications.

The beginning of the era of scientific chemistry was marked by the synthesis of large numbers of dyes for textile related purposes. Some of these were also applied to inorganic substrates by adsorption, for use as pigment toners. The commercially available soluble sodium salts of acid dyes were rendered insoluble, an essential property of pigments, by reacting them with the water-soluble salts of calcium, barium, or lead to form lakes. Basic dyes (commercially available as chlorides or as
other water-soluble salts), on the other hand, were treated with tannin or antimony potassium tartrate to yield insoluble colourants, that is, pigments. Some of the early commercially important lakes, such as Lake Red C (Pigment Red 53:1) and Lithol Rubine (Pigment Red 57:1), released on to the market in 1902 and 1903, respectively, are still commercially important products (Section 2.7).

Entering the market in the late nineteenth century were the first water insoluble pigments that did not contain acidic or basic groups, namely, the red β-naphthol pigments (Para Red P.R.1, 1885). Falling into the same chemical class are Toluidine Red (P.R.3, 1905) and Dinitroaniline Orange (P.O.5, 1907), two members of this class of pigments that still enjoy commercial importance today. In 1909, Hansa Yellow (P.Y.1) was introduced to the market as the first monohydrazone yellow pigment. The first red Naphthol AS pigments followed in 1912, and the first commercial pioneers of the diarylide yellow pigment range, some of which had been patented as early as 1911 [2], appeared in 1935. Phthalocyanine blue pigments also appeared in 1935, followed by phthalocyanine green pigments a couple of years later [3]. The rapid advances in pigment chemistry led to such important classes of pigments as dihydrazone condensation pigments in 1954, quinacridones in 1955, dihydrazone pigments of the benzimidazolone series in 1960, the isoindolinone pigments in 1964 [4], and the diketopyrrolopyrrole pigments in 1986.

1.3 Classification of Organic Pigments

Several classification systems for organic pigments have been proposed over the years. Basically, it seems appropriate to adopt a classification system by grouping pigments either by chemical constitution or by colouristic properties. A strict separation of the two classification systems is not very practical, because the categories tend to overlap; however, for the purposes of this book it is useful to list pigments according to their chemical constitution.

A rough distinction can be made between hydrazone and nonhydrazone pigments. Most nonhydrazone pigments have polycyclic ring systems and are therefore known as polycyclic pigments. The group of hydrazone pigments can be further subdivided according to structural characteristics, such as by the number of hydrazone groups or by the type of diazo or coupling component. Polycyclic pigments, on the other hand, may be identified by the number and the type of rings that constitute the aromatic structure. Furthermore, there is a smaller group of pigments that contains neither a hydrazone moiety nor a polycyclic ring system.

1.3.1 Hydrazone Pigments (Formerly Called Azo Pigments) (Chapter 2)

Hydrazone pigments have the hydrazone group (–NH–N=) in common. Formerly, hydrazone pigments were called ‘azo pigments’, because they were believed to contain the azo group –N=N–. However, all commercial ‘azo’
pigments do not contain an azo group, but a hydrazone group instead (see Chapter 2, Section 2.1 for details). Thus, the correct name is 'hydrazone pigments' instead of 'azo pigments', and this name is used throughout this book.

The synthesis of hydrazone pigments is economically attractive, because the standard sequence of diazonium salt formation and subsequent reaction with a wide choice of coupling components allows access to a wide range of products. The hydrazone pigments can be subdivided into monohydrazone and dihydrazone pigments.

1.3.1.1 Monohydrazone Yellow and Orange Pigments (Formerly Called Monoazo Yellow and Orange Pigments) (Section 2.3)
Monohydrazone yellow pigments that are obtained by coupling a diazonium salt with acetoacetic arylides as coupling components cover the spectral range between greenish and medium yellow; coupling with 1-arylpyrazolones-5 affords reddish yellow to orange shades.

All members of this pigment family share good lightfastness, combined with poor solvent and migration resistance. These properties define and limit their application. Monohydrazone yellow pigments are used extensively in air-dried alkyd resin and in emulsion paints, and certain inks used in flexo and screen printing. Other applications are in letterpress and offset inks, as well as in office articles.

1.3.1.2 Dihydrazone Pigments (Formerly Called Disazo Pigments) (Section 2.4)
There is a dual classification system based on differences in the starting materials. The first and most important group includes compounds whose synthesis involves the coupling of di- and tetra-substituted diaminodiphenyls as diazonium salts with acetoacetic arylides (diarylide yellows) or pyrazolones (dihydrazone pyrazolones) as coupling components. The second group, bisacetoacetic arylide pigments, are obtained by diazotization of aromatic amines, followed by coupling to bisacetoacetic arylides.

The colour potential of dihydrazone pigments covers the colour range from very greenish yellow to reddish yellow and orange and red. Most show poorer lightfastness and weatherfastness – but better solvent and migration fastness than monohydrazone yellow and orange pigments. Their main applications are in printing inks and plastics, and to a lesser extent in coatings and toners for laser printing.

1.3.1.3 β-Naphthol Pigments (Section 2.5)
β-Naphthol pigments provide colours in the range from orange to medium red. The typical coupling reaction with β-naphthol as a coupling component yields such well-known pigments as Toluidine Red and Dinitroaniline Orange. Their commercial application in paints requires good lightfastness. Solvent resistance, migration fastness and lightfastness are comparable to the monohydrazone yellow pigments.

1.3.1.4 Naphthol AS Pigments (Section 2.6)
These pigments are obtained by coupling substituted aryl diazonium salts with arylides of 2-hydroxy-3-naphthoic acid (2-hydroxy-3-naphthoic acid anilide =
Naphthol AS). They provide a broad range of colours from yellowish and medium red to bordeaux, carmine, brown and violet; their solvent fastness and migration resistance are only marginal. Naphthol AS pigments are used mainly in printing inks and paints.

1.3.1.5 Hydrazone Pigment Lakes (Formerly Called Azo Pigment Lakes) (Section 2.7)
In Europe, pigments of this type are known as ‘toners’, but since this term is used differently elsewhere we refer to them as ‘lakes’ throughout this book, although a chemically correct description would be ‘salt type pigments’.

Historically, ‘lakes’ referred to the first type of synthetic organic pigments made from water-soluble dyes by precipitation onto alumina hydrate (aluminium hydroxide).

Laked pigments are formed by precipitating a monohydrazone compound that contains sulfo and/or carboxy groups. The coupling component in the reaction may vary: monohydrazone yellow pigment lakes are based on acetoacetic arylides or 1-arylpyrazolones-5 (Section 2.3.1.2); β-naphthol lakes are derived from 2-naphthol; BONA pigment lakes use 2-hydroxy-3-naphthoic acid (Beta-Oxy-Naphthoic Acid); and Naphthol AS pigment lakes contain anilides of 2-hydroxy-3-naphthoic acid as a coupling component. Lakes may also be prepared from naphthalenesulfonic acids.

Monohydrazone yellow pigment lakes show good migration fastness and heat stability, making them useful products for plastics. Lake Red C is one of the commercially significant β-naphthol lakes. Limited lightfastness, which ranks far behind the non-laked β-naphthol counterparts, along with a tendency to migrate largely restricts their use mainly to the printing inks field.

Most BONA lake pigments provide an extra site for salt formation. Apart from the usual substituents, the diazo components of almost all BONA lake pigments contain a sulfonic acid function. Two acid substituents are thus available to form insoluble salts, which is the form in which these pigments are commercially available. Metal cations such as calcium, strontium, barium, magnesium or manganese combine with the organic anion to produce shades between medium red and bluish red. Their use in printing inks exceeds their increasing use in plastics and paints.

The organic acid group of Naphthol AS pigment lakes is part of the diazo component; a second site for salt formation can be provided by the coupling component. The plastics industry is the main user of such lakes.

Naphthalenesulfonic acid lake pigments are based on naphthalenesulfonic acid as a coupling component; introduction of an additional $SO_3H$ function as part of the diazo component is possible.

1.3.1.6 Benzimidazolone Pigments (Section 2.8)
Benzimidazolone pigments feature the benzimidazolone structure, introduced as part of the coupling component. The pigments that are obtained by coupling to 5-acetoacetylaminobenzimidazolone cover the spectrum from greenish yellow to orange; 5-(2-hydroxy-3-naphthoylamino)benzimidazolone as a coupling component affords products that range from medium red to carmine, maroon,
bordeaux and brown shades. Pigment performance, including lightfastness and weatherability, is generally excellent. Pigments that satisfy the specifications of the automobile industry are used to an appreciable extent in automotive finishes. Benzimidazolone pigments are also used extensively to colour plastics and high grade printing inks.

1.3.1.7 Dihydrazone Condensation Pigments (Formerly Called Disazo Condensation Pigments) (Section 2.9)
These pigments can formally be viewed as resulting from the condensation of two carboxylic monohydrazone components with one aromatic diamine. The resulting high molecular weight pigments show good solvent and migration resistance and generally provide good heat stability and lightfastness. Their main markets are in the plastics field and in spin dyeing. The spectral range of dihydrazone condensation pigments extends from greenish yellow to orange and bluish red or brown.

1.3.2 Polycyclic Pigments (Chapter 3)
Pigments with condensed aromatic or heterocyclic ring systems are known as polycyclic pigments. The numerous pigment classes that fall into this category do not reflect their actual commercial importance; only a few are produced in large volumes. Their chief characteristics are good light- and weatherfastness and good solvent and migration resistance, but, apart from the phthalocyanine pigments, they are generally also more costly than hydrazone pigments.

1.3.2.1 Phthalocyanine Pigments (Section 3.1)
Phthalocyanine pigments are derived from the phthalocyanine structure, a tetraaza-tetrabenzoporphine. Although this basic molecule can chelate with a large variety of metals under various coordination conditions, today only the copper(II) complexes are of practical importance as pigments. Excellent general chemical and physical properties, combined with good economy, make them the largest fraction of organic pigments in the market today. Copper phthalocyanine blue exists in several crystalline modifications. Commercial varieties include the reddish blue alpha form, as stabilized and nonstabilized pigments, the greenish blue beta modification and, as yet less important, the intense reddish blue epsilon modification. Bluish to yellowish shades of green pigments may be produced by introduction of chlorine or bromine atoms into the phthalocyanine molecule.

1.3.2.2 Quinacridone Pigments (Section 3.2)
The quinacridone structure is a linear system of five anellated rings. These pigments largely have the same performance attributes as phthalocyanine pigments. Outstanding light- and weatherfastness, resistance to solvents and migration resistance justify the somewhat higher market price in applications for high grade industrial coatings, such as automotive finishes, for plastics and special
printing inks. Unsubstituted trans-quinacridone pigments are commercially available in a reddish violet beta and a red gamma crystal modification. One of the more important substituted pigments is the 2,9-dimethyl derivative, which affords a clean bluish red shade in combination with excellent fastness properties. Solid solutions of unsubstituted and differently substituted quinacridones and blends with quinacridone quinone resulting in reddish to yellowish orange pigments are commercially available; in contrast, 3,10-dichloroquinacridone as yet enjoys only limited success as a pigment.

1.3.2.3 **Perylene and Perinone Pigments** (Section 3.4)
Perylene pigments include the dianhydride and diimide of perylene tetracarboxylic acid along with derivatives of the diimide; while perinone pigments are derived from naphthalene tetracarboxylic acid.

Commercially available types provide good to excellent lightfastness and weatherability; some of them, however, darken upon weathering. A number of them have excellent heat stability, which renders them suitable for spin dyeing. They are also used to colour polyolefins that are processed at high temperatures. The list of applications includes high grade industrial coatings, such as automotive finishes, and, to a lesser degree, special printing inks for purposes such as metal decoration and poster printing.

1.3.2.4 **Diketopyrrolopyrrole (DPP) Pigments** (Section 3.5)
The basic skeleton of this group of pigments consists of two anellated five-membered rings each of which contains a carbonamide moiety in the ring.

This class of pigments presently has some commercially used representatives, one of them with great importance in the market. In full shades and white reductions, the pigments afford shades in the colour range from orange to medium and bluish reds. The pigments are used primarily in high grade industrial coatings, including automotive finishes and in plastics because of their excellent lightfastness and weatherfastness as well as their good heat stability.

1.3.2.5 **Thioindigo Pigments** (Section 3.6)
4,4',7,7'-Tetrachlorothioindigo with a reddish violet shade reigns supreme as a pigment amongst the derivatives of this indigo. It can be used for bordeaux shades in automotive refinishes. Thioindigo pigments are generally used in industrial coatings and plastics for their good lightfastness and weatherfastness in deeper shades.

1.3.2.6 **Pigments Derived from Anthraquinone** (Section 3.7)
Apart from some nonclassified pigments such as Indanthrone Blue (P.Bl.60), the anthraquinone pigments, which are structurally or synthetically derived from the anthraquinone molecule, can be divided into the following four groups of polycyclic pigments.

1.3.2.6.1 **Anthrapyrimidine Pigments**
The commercially leading member of this class is Anthrapyrimidine Yellow, which in very light white reductions affords a greenish to medium yellow with
excellent weatherfastness. It lends itself primarily to application in industrial coatings such as automotive metallic finishes or to modification of the shades of automotive finishes.

1.3.2.6.2 **Flavanthrone Pigments**
Flavanthrone Yellow, the only commercially used flavanthrone, is a moderately brilliant reddish yellow. Excellent lightfastness and weatherfastness, combined with good solvent and migration resistance, make this pigment an attractive supplement to Anthrapyrimidine Yellow, mainly in the automotive finish industry.

1.3.2.6.3 **Pyranthrone Pigments**
Commercial attention focuses on the derivatives of the pyranthrone molecule at a varying level of halogenation. Most are orange, but others exhibit a dull medium to bluish red shade. Owing to their good weatherfastness pyranthrone pigments are used for high grade industrial finishes.

1.3.2.6.4 **Anthanthrone Pigments**
Dibromoanthanthrone is the only commercial pigment within this group. Qualities such as outstanding light- and weatherfastness justify the relatively high cost for application in high grade industrial coatings such as automotive finishes. The transparent pigment provides shades of scarlet for metallic finishes.

1.3.2.7 **Dioxazine Pigments (Section 3.8)**
Dioxazine pigments are based on triphenodioxazine, a linear system of five annelated rings. Apart from Pigment Violet 37, the commercially most representative one is Pigment Violet 23, an extremely lightfast and weatherfast compound with good to excellent solvent and migration resistance. Applications include the pigmentation of coatings, plastics, printing inks, as well as spin dyeing. Apart from producing violet shades, the pigment also lends itself to the shading of phthalocyanine blue pigments in colourations, particularly in coatings. It is also used to tone the light yellowish shade of titanium dioxide in whites and in shading carbon blacks that have a brownish cast.

1.3.2.8 **Quinophthalone Pigments (Section 3.9)**
Quinophthalone pigments have a polycyclic structure derived from quinaldine and phthalic anhydride. A few members of this class have gained commercial recognition for their very good temperature resistance. The main markets for their mostly greenish yellow shades are in the plastics and coatings industries.

1.3.2.9 **Isoindolinone and Isoindoline Pigments**
Although of comparatively good light- and weatherfastness and solvent and migration resistance, only a few members of the isoindolinone and isoindoline families are commercially available as pigments. Chemically classified as heterocyclic azomethines, these pigments produce greenish to reddish yellow hues. Isoindolinone pigments are preferably supplied for the pigmentation of plastics and high grade coatings.
1.3.3

Miscellaneous Pigments (Chapter 4)

There are a few pigment classes that can neither be sorted under hydrazone nor under polycyclic pigments. This group includes triarylcyanium pigments and metal complex pigments as well as a number of individual pigments not belonging to a larger class of commercial pigments.

1.3.3.1 Triarylcyanium Pigments (Section 4.1)
There are two groups of triarylcyanium pigments: (i) inner salts of triphenylmethane sulfonic acids and (ii) complex salts with heteropolyacids containing phosphorus, tungsten, molybdenum, silicon or iron.

The first group is characterized by poor lightfastness and limited solvent resistance. Alkali Blue is the only member of this group with considerable commercial value. To tone black printing inks, Alkali Blue is used in combination with the very high-absorbing carbon black pigment, which increases its lightfastness considerably.

The second group includes the complex salts of basic pigments that are common in the dyes industry, such as Malachite Green, Methylene Violet, Crystal Violet or Victoria Blue with certain heteropolyacids. Despite the disadvantages of comparatively poor solvent resistance and limited lightfastness, these pigments are used for their excellent colour brilliance and clarity of hue – properties that exceed those of any of the other known organic or inorganic pigments. Such features make these types, whose lightfastness satisfies commercial requirements, suitable candidates for the printing inks industry and especially for packaging inks.

1.3.3.2 Metal Complex Pigments (Section 4.2)
Most metal complex pigments contain either an azo group (−N=N−) or an azomethine (−CH=N−) moiety. The metal is usually nickel or copper, and less commonly cobalt or iron(II).

Only a few azo metal complexes are available as pigments. They exhibit green or greenish yellow shades. Most of these are very lightfast and weatherfast.

Commercial azomethine complex pigments afford yellow, orange or red shades. Those species that provide the required lightfastness and weather resistance are used in automotive finishes and other industrial coatings.

1.4

Relationship between Chemical Structure and Pigment Properties

In this chapter, the correlation between chemical constitution and pigment performance is outlined in terms of empirical rules. These correlations are essentially applicable, independently of the application medium, to all industrial uses of pigments.

While the properties of (soluble) dyes are determined almost exclusively by their chemical constitution, application characteristics of pigments – which are
by definition insoluble in the medium in which they are applied (Section 1.1) – are largely controlled by their crystalline constitution, that is, by their physical characteristics. This is discussed in the next chapter.

The application properties of a pigment are basically governed by its chemical constitution, which in turn has a bearing on the crystal structure, thus determining the physical parameters. This seemingly straightforward correlation is complicated by the fact that various crystal structures (modifications, see Section 1.5.3) may evolve from one and the same chemical constitution. Apart from knowledge about the chemical constitution of a compound, only extensive insight into the crystal structures and their solid-state physics thus allows certain predictions as to the application properties of the pigment.

This chapter discusses the influence of the chemical constitution on the hue, tinctorial strength, lightfastness, weatherfastness, solvent resistance, and migration resistance of a pigment. The systematic synthesis of a pigment with certain defined target properties is only possible to a very limited extent. Only with a reliable crystal-structure prediction can a prediction of the pigment’s properties be made.

1.4.1 Hue

The appearance of colour in a molecule is associated with electronic excitation [5–9] caused by absorption of incident electromagnetic radiation in the ultraviolet and visible regions of the spectrum. Electrons are elevated from the ground state energy level to an excited state by absorbing selected frequencies of incident visible light, thereby giving the molecule the shade of the resulting complementary colour. The fact that each electronic excitation is accompanied by a battery of rotational and vibrational transitions is responsible for the appearance of more or less broad absorption bands. An absorption band is said to undergo a bathochromic shift if a comparison of spectra shows that it has moved to longer wavelengths; a hypsochromic shift involves movement to shorter wavelengths.

The hue is primarily defined by the pattern of chromophores, a conjugated π-system, which is responsible for the absorption of visible light. For transition-metal containing compounds, for example copper phthalocyanine, the electrons of the metal play a role, too.

Substituents with lone electron pairs, such as alkoxy, hydroxy, alkylamino and arylamino groups, are known as electron donors. Alkyl groups, despite the absence of such free electron pairs, are also considered to be electron donors. Functional groups with conjugated π-electron systems, such as NO$_2$, COOH, COOR, SO$_2$NH$_2$ or SO$_2$Ar, act as electron acceptors.

In discussing substituents of hydrazone pigments, both electron donors and electron acceptors are effective particularly as parts of the diazo component; that is, they are located in the conjugated part of the system. In these positions they usually cause a bathochromic shift of the absorption band with the longest
wavelength. Evaluation of the empirical bathochromic effects of differently substituted derivatives against a standard conjugated system can provide a sequence of increasingly effective substituents. In azobenzene systems, for instance, electron donors are more bathochromically active than electron acceptors. Since this effect, however, also depends on the electron distribution between donor, acceptor and hydrazone function, a (usually less pronounced) hypsochromic shift may be observed, especially if electron acceptors are involved. Bathochromic or hypsochromic behaviour is also determined by the electron distribution at the substituted site within the conjugated system. If a bonding electron pair is promoted to a nonbonding excited state, a $\pi \rightarrow \pi^*$ transition ensues that determines the frequency of the dominant absorption with the longest wavelength.

The intensity of an $n \rightarrow \pi^*$ transition (transition of one electron of a lone electron pair from a nonbonding (n) to an antibonding ($\pi^*$) orbital) is about two magnitudes less than the dominant $\pi \rightarrow \pi^*$ transitions and thus has no effect on the colour.

Today, the Witt substitution rules, originally derived from empirical data on conjugated systems such as hydrazone derivatives, can be approached quantum mechanically. Hydrazine pigments basically obey the rules for azo dyes, although deviations through interactions within the crystal lattice must be taken into account.

The basic hue of a hydrazine pigment is primarily defined by the structure of the coupling component, since pigment manufacturers focus almost exclusively on substituted anilines as diazo components. Shades of yellow, for instance, are preferably produced by using acetoacetic arylides ($\text{CH}_3\text{COCH}_2\text{CONH-Ar}$) or heterocyclic coupling components based on the structure:

![Hydrazine structure](image)

in a cyclic conformation. Products include barbituric acid (1) or 2,4-dihydroxyquinoline (2). Such compounds absorb mainly in the short wave (blue) region of visible light. The reddish yellow to orange shades produced by monohydrazone pigments obtained from 1-arylpurazolone-5 derivatives (3) as coupling components have to be considered as exceptional.

A more bathochromic redshift is provided by monohydrazone pigments featuring the enlarged conjugated system of 2-hydroxynaphthalene ($\beta$-naphthol), particularly its 3-carboxylic acid and 3-carboxylic aryde derivatives.
Diazotized aromatic amines may also be of some significance in defining absorption frequencies. An amine with a considerably enlarged conjugated system, made, for instance, by dimerization, can contribute to a considerable bathochromic shift. Examples include the following:

<table>
<thead>
<tr>
<th>Diazotized component</th>
<th>Coupling component</th>
<th>Shade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline derivatives</td>
<td>&gt; Pyrazolone-5-derivatives</td>
<td>Yellow to orange</td>
</tr>
<tr>
<td>3,3’-Dichlorobenzidine</td>
<td>&gt; Pyrazolone-5-derivatives</td>
<td>Yellowish red</td>
</tr>
<tr>
<td>Aniline derivatives</td>
<td>&gt; Naphthol AS derivative</td>
<td>Red</td>
</tr>
<tr>
<td>3,3’-Dichlorobenzidine</td>
<td>&gt; Naphthol AS derivative</td>
<td>Violet to blue</td>
</tr>
</tbody>
</table>

Hydrazone pigments range in shade from greenish yellow to orange, red, blue, violet and brown. The chemical constitution of the pigment, especially the substitution pattern of the coupling component, determines the basic colour of a pigment; different shades within this colour are influenced by the crystal structure and by physical characteristics, such as particle size and morphology.

Substitution patterns, especially that of the diazotized aromatic amine, determine the colour of a pigment to some extent; however, empirical data do not lead to unambiguous conclusions as to the exact influence of a particular substituent on the shade. The problem is intricate, since the substitution pattern also has a bearing on the crystal structure, including all the interactions associated with it.

An exchange of substituents on the arylide moiety of the coupling component (arylides of acetoacetic acid and 2-hydroxy-3-naphthoic acid) fails to afford a consistent influence on the shade. In this case, intramolecular and intermolecular interactions within the crystal lattice gain more significance, since the conjugation of π-electrons is not expected to extend far beyond the carbonamide bridge.

The same general considerations apply to polycyclic pigments.

The insertion of heteroatoms into a polycyclic system, on the other hand, is frequently accompanied by a hypsochromic shift, due to a larger distance between the level of the highest occupied (HOMO) and the level of the lowest unoccupied molecular orbital (LUMO) (more exactly: due to the higher energy difference between the ground state and the ππ* state). Thus, for example:
The colouristic effect of substituting a polycyclic pigment system is expected to parallel that afforded by employing substituted diazo components in the manufacture of hydrazone pigments. Considerable chlorine substitution may even change the basic colour of a pigment. In contrast to the blue copper phthalocyanine pigments, copper polychloro-phthalocyanine pigments appear in green shades (Section 3.1); the chlorine atoms of tetrachloroisoiindolinone pigments shift the absorption bands from the yellow region towards orange or red (Section 3.10).

The hue of a red hydrazone pigment lake carrying sulfonic acid functions is determined to a considerable extent by the metal ion. In the series of Na, Ba, Sr, Ca and Mn the shift of hue from yellowish to bluish red increases in the order in which they are listed. In addition, the polymorphic form and the hydration state may have a strong effect on the hue.

Particularly large colour changes are associated with the transition from solution to solid state in heterocycles such as the cross-conjugated indigo system or the quinacridone skeleton. Quinacridone pigments, dissolved in hot DMSO (dimethyl sulfoxide) or in DMF, exhibit a pale yellow shade; the intense red colour appears only in the solid state. This is a particularly distinctive example that demonstrates the correlation between crystal-lattice interactions and hue [10]. (For details see Section 1.5.3.)

Various methods have been developed to calculate and predict absorption spectra of hydrazone and polycyclic compounds by quantum mechanics. However, the investigation of solid state spectra is complicated by interactions within the crystal lattice, which make accurate calculations of optical properties a challenging task.

1.4.2 Tinctorial Strength

Since the colour strength of a pigment is defined by its tendency to absorb light, the maximum molar extinction coefficient \( \varepsilon_{\text{max}} \) can be used to estimate the relative strength of a pigment, which is, however, also dependent on the physical parameters of the pigment crystal (Section 1.5). A better approach is to measure the absorption connected with a single electron transition, especially the one with the longest wavelength, and to integrate the peak between the lower limit \( \nu_1 \) and the upper limit \( \nu_2 \) to calculate the total area \( f \) under the peak:

\[
f = \int_{\nu_1}^{\nu_2} s_\nu \, d\nu
\]

This is known as the oscillator strength. For practical purposes, \( \varepsilon_{\text{max}} \Delta \nu_{\frac{1}{2}} \) with \( \Delta \nu_{\frac{1}{2}} \) being the full-width at half-maximum, provides a good approximation. To be precise, the term oscillator strength refers to a free molecule or, as a first approximation, to a molecule in a solvent that does not noticeably interact with the chromophore system. Thus, for all practical purposes, it seems much more useful to approach the problem by focusing on the correlation between extinction and molecular parameters.

The primary chemical aspect of a mesomeric pigment system concerns the correlation between tinctorial strength and extent of electron delocalization.
3.7.4.1.4 Pigment Red 226

Pigment Red 226 (Scheme 3.20) is a dibromo-6,14-dichloro-pyranthrone. It provides a medium, somewhat dull red shade, which is considerably more bluish than that of P.O.51. The shade, although noticeably duller, corresponds to that of the less fast toluidine red pigments. P.R.226 is distinctly yellower than P.R.216. Despite the fact that P.R.226 demonstrates good fastness to solvents, it is much less resistant than other members of its class. The difference is most noticeable in toluene and xylene. P.R.226 is fast to acids and alkali. Like P.O.51, it is thermally stable up to more than 200°C, even in long-term exposure for several weeks. The commercial grade is more transparent than P.O.51 and provides excellent lightfastness and weatherfastness. P.R.226 is a special-purpose type that is used for metallic finishes. It is a suitable pigment for automotive finishes, especially for two-coat metallic finishes, quite often in combination with UV absorbants in the clean top coat.

3.7.4.2 Anthanthrone Pigments

Anthanthrone pigments are characterized by the basic structure 86:

![Anthanthrone structure](image)

The unsubstituted ring system, although exhibiting an orange shade, apart from other deficiencies is tinctorially not strong enough to stimulate interest. Only halogenated derivatives have gained some interest throughout the pigment industry.

Anthanthrone is synthesized from naphthostyril (87), which is saponified to form 1-aminonaphthalene-8-carboxylic acid (88). Naphthostyril itself is prepared from 1-naphthylamine with phosgene in the presence of dry aluminium chloride.

Diazotizing 88 and boiling the solution in the presence of copper powder affords 1,1'-dinaphthyl-8,8'-dicarboxylic acid (89), which is cyclized with aluminium chloride, but preferably with concentrated sulfuric acid at 30–40°C, to produce anthanthrone (86):
The Friedel–Crafts reaction, which proceeds via electrophilic aromatic substitution, as illustrated in the following scheme, is unique to the manufacture of anthanthrone pigments. Most other polycyclic anthraquinone pigments are synthesized via nucleophilic ring closure.

4,10-Dibromoanthanthrone (90) is registered as Pigment Red 168, C.I. 59300. First synthesized as early as 1913 as a vat dye, this compound is the commercially most interesting halogenated anthanthrone derivative:

Scheme 3.21 Molecular structure of P.R.168.

Compound 90 may be prepared directly from 86 without intermediate isolation of 86 by treating the dicarboxylic acid 89 with monohydrate or with concentrated sulfuric acid at 35 °C, followed by bromination in the presence of iodine as a catalyst.

P.R.168 exists in two polymorphic forms [185]. The metastable β-polymorph is formed upon synthesis. This orange product is mainly used as a vat dye. Finishing, for example by recrystallization from sulfuric acid, leads to the thermodynamically stable scarlet α-phase, which is used as a pigment.

In the α-phase of P.R.168 the molecules adopt a ‘brick’ packing, as it is also found in the β-phase of P.R.224 (Figure 3.64). While the molecules arrange in a herringbone arrangement in P.R.168, they form slightly wavy layers in P.R.224 (Figure 3.65). Similarly as in P.R.224, the molecular packing is extremely efficient and dense (Figure 3.66).

In contrast to the reddish orange colour of P.R.168, which is referred to as scarlet, the yellower 4,10-dichloroanthanthrone is of no commercial interest as a pigment and is therefore no longer produced.

3.7.4.2.1 Commercially Available Anthanthrone Pigments

3.7.4.2.1.1 Pigment Red 168

Pigment Red 168 dibromoanthanthrone, is a vat type pigment that demonstrates excellent fastness properties, a feature that is an asset in high grade paints.
Figure 3.64  Comparison of the crystal structures of (a) P.R.168 (α-phase) and (b) P.R.224 (β-phase); view along the stacking direction.

Figure 3.65  Comparison of the crystal structures of (a) P.R.168 (α-phase) and (b) P.R.224 (β-phase); view perpendicular to the stacking direction.
It provides a clean yellowish shade of scarlet, somewhere between that of P.O.43, a naphthalene tetracarboxylic acid derivative, and those of yellowish perylene tetracarboxylic acid type pigments.

P.R.168 is entirely or almost entirely resistant to most of the organic solvents commonly found in typical binder systems. P.R.168, like other vat type pigments, is not completely fast to overcoating in oven drying systems that are baked at 120–160°C. The degree of bleeding depends on the individual system. The pigment is thermally stable up to 180°C. It is one of the most lightfast and weatherfast organic pigments known. Excellent performance standards make it a suitable candidate for all types of coatings and paints, even at very low pigment concentrations. P.R.168 is used both as a shading pigment and in mixed systems. It exhibits comparatively low tinctorial strength. The commercial products, like those of other vat type pigments, are more or less transparent, which makes them useful products for metallic finishes. P.R.168 is used, for instance, in one- and two-coat automotive finishes. Moreover, it is weatherfast enough to be used in low concentrations. In such systems, P.R.168 is also employed in combination with highly fast, typically reddish yellow pigments to produce shades of bronze and copper. The pigment is equally useful in conjunction with more reddish

Figure 3.66  Perfect space filling in the crystal structure of P.R.168 (α-phase).
3.7.4 Polycarbocyclic Anthraquinone Pigments

organic pigments, such as with perylenetetracarboxylic acid pigments. High weatherfastness makes it a suitable candidate for use in architectural paints and in emulsion paints, including those targeted for outdoor use. The fact that P.R.168 is only used in very light tint allows its comparatively high price in this market. Specialized pigment preparations are also available for these purposes. P.R.168 is fast to alkali and plaster. The pigment is also recommended for use in coil coating, including PVC coatings (Section 1.8.2.2).

P.R.168 is found to a lesser extent in printing inks and plastics. The printing ink industry utilizes P.R.168 to produce special-purpose printing inks, which may be applied to substrates such as posters or metal deco prints. The pigment demonstrates equally excellent fastness in these materials. 1/1 SD systems equal step 8 on the Blue Scale for lightfastness, while 1/3 to 1/25 SD formulations match step 7. The prints are resistant to common organic solvents and chemicals. The pigment is thermally stable up to 220°C for 10 min, and its prints may safely be sterilized.

3.7.4.2.1.2 Pigment Orange 77

The pigment is listed in the Colour Index under Constitution Number 59105:

![Scheme 3.22 Molecular structure of P.O.77.](image)

It is described as bright yellowish orange and can be used for aqueous flexo inks and in the plastics application in dibutyl phthalate paste as plasticiser for PVC. Dyeing of technical leathers is as well described.

3.7.4.3 Isoviolanthrone Pigments

Isoviolanthrone (91) is an highly anellated polycyclic quinone system. It is derived from the chemical structure of isodibenzanthrone, which may be visualized as being obtained by unsymmetrical condensation of two benzanthrone (92) molecules. The compound isoviolanthrone itself affords an intense blue shade.