H23: Types of Colorant

The first materials to be used as colorants were used in cave paintings over twenty thousand years ago. These colorants were all of natural origin being based on coloured minerals, crushed bones, chalk and soot. The range of early colouring materials was expanded by the Egyptians who introduced dyes such as blue indigo and pigments such as natural ultramarine. Further introductions were made by the Greeks and Romans who experimented with chemistry to produce new colorants, but the range of dyes and pigments available was still very limited by modern standards.

It was only with the advent of synthetically produced colorants and more specifically the discovery of mauveine by Perkin in 1856 that the number of colorants began to significantly increase.

Origins of colour

The most common mechanism of creating colour is the selective absorption of light wavelengths, occurring in most dyes or pigments used in creating surface colours. Examples of the use of light absorption in creating colour might be dyed fabrics, paint layers, pigmented plastics or printed card. Some pigments also scatter light, giving rise to opacity as the scattered light does not reach through to the far side of the layer. More "exotic" mechanisms of colour creation are interference (which gives rise to colours in insect wings, colours in oil in puddles and is now being used in novel car paints) and luminescence, as shown by the phosphors in television screens. You may be surprised to learn that there are actually fifteen causes of colour, which are summarised in Table 1:

Table 1: The fifteen causes of colour

Vibrations and Simple Excitations		
1	Incandescence	Flames, carbon arc, limelight
2	Gas Excitations	Vapour lamps, lightning, auroras, some lasers
3	Vibrations / Rotations	Ice, iodine, blue gas flame
Transitions involving Ligand Field Effects		
4	Transition Metal Compounds	Many pigments, turquoise, phosphors
5	Transition Metal Impurities	Ruby, emerald, some fluorescence
Transitions between Molecular Orbitals		
6	Organic Compounds	Most dyes, some fluorescence, some lasers
7	Charge Transfer	Many pigments, blue sapphire, lapis lazuli
Transitions involving Energy Bands		
8	Metals	Copper, silver, gold, brass
9	Pure Semiconductors	Silicon, diamond
10	Doped Semiconductors	Blue and yellow diamond, light-emitting diodes
11	Colour Centres	Amethyst, smoky quartz
Geometrical and Physical Effects		
12	Dispersive Refraction / Polarisation	Rainbows, halos, "fire" in gemstones
13	Scattering	Blue sky, red sunset, blue eyes, moonstone
14	Interference	Oil on water, soap bubbles, insect wings
15	Diffraction	Opal, diffraction gratings

Taken from: "The Physics and Chemistry of Color: The Fifteen Causes of Colour"
Kurt Nassau, John Wiley & Sons, 1983.

These fifteen mechanisms are defined in terms of the change within the system that gives rise to the colour seen. However, when we are using coloured materials to create a particular effect, all we are interested in is the effect the material has on the light incident upon it. The system may absorb, scatter or reflect the light; it may also cause effects such as interference or fluorescence. For example, light shining on a glossy print layer will be partially reflected at the surface, partially absorbed and scattered by the pigments present in the layer, and either absorbed or reflected by the underlying substrate layer.
Classification of colorants

Dye or pigment

The Society of Dyers and Colourists (SDC) define a dye as:

"A substance, usually organic, which is designed to be absorbed or adsorbed by, made to react with, or deposited within a substrate in order to impart colour with some degree of permanence."

You will see from this definition that there is no mention of the property of solubility, however it is generally accepted that a dye will exist in solution during part of the coloration process. Dyes are generally used in the coloration of textiles, although other substrates such as paper and leather may also be dyed.The word "pigment" derives from the Latin pigmentum – pingere, to paint. The Color Pigments Manufacturers Association of America (CPMA), formerly known as Dry Color Manufacturers Association of America (DCMA), has defined pigments in the following way:

"Pigments are colored, black, white or fluorescent particulate organic or inorganic solids, which are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or scattering of light.
Pigments are usually dispersed in vehicles or substrates for application, as for instance in the manufacture of inks, paints, plastics, or other polymeric materials. Pigments retain a crystal or particulate structure throughout the coloration process."

These definitions classify the material according to how the material is used. This is absolutely correct, as the same chemical compound can be used as a pigment or as a vat dye; it is the application process that determines whether the colorant is a dye or a pigment.

There are about 5,000 compounds classified as dyes in the "Colour Index" and about 400 compounds classified as pigments.

Pigment classification

In 1920 the UK Dyer's Company (now transformed into the Society of Dyers and Colourists SDC) began devising 'some means or other to systematise the nomenclature of the colours'. Plans for the Colour Index were announced in 1921 and by 1924 the first volume had been produced. The Colour Index has been updated many times and, when the second edition was published in 1956, became the standard reference work for the listing and classification of colorants.

The aims of any colorant classification system should be to allow clear identification and description of colorants to aid people wishing to select and use colorants. The most common categories for pigment classification are based on chemical constitution, as illustrated in Figure 1.

Figure 1: Classification of pigment types
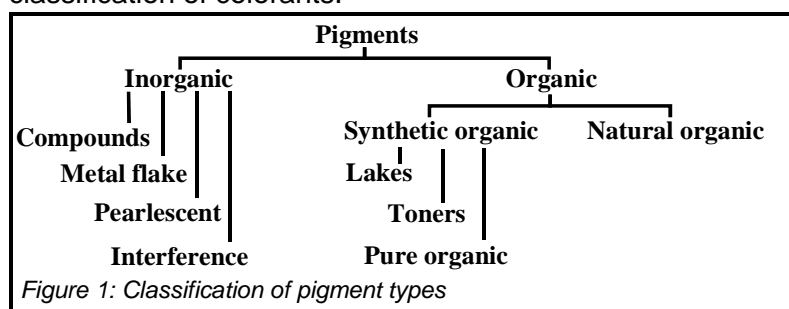
Inorganic pigments

The coloured oxides, sulphides, hydroxides, sulphates, carbonates etc of metals. Metal flake pigments, pearlescent pigments and interference pigments

Organic

Molecules based primarily on aromatic carbons for the backbone structure.

A further division of this category can be made by splitting the pigments into groups depending on how they are obtained produced:

Natural

Pigments obtained from a natural source such as yellow ochre. Natural organic pigments are a minority group and used only for specialist applications.

Synthetic

Organic pigments that are chemically manufactured. These are commercially the most important pigments.

Further classification of pigments can be made by splitting the pigments into colour groups, for example by classifying all red inorganic pigments into the same group.
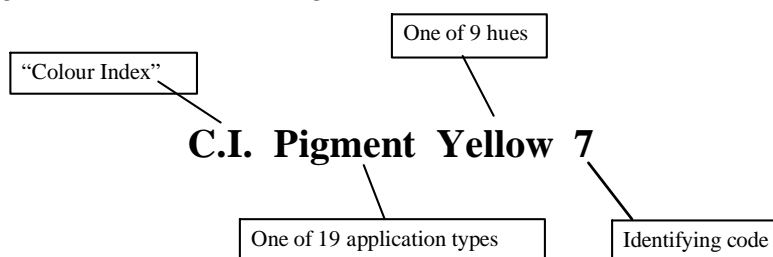
Each colorant is assigned a C.I. Generic Name and a Chemical Constitution Number.

Generic name:

Gives the nature of the product, the colour and a chronological number

Chemical constitution number:

A five-figured number that is assigned to a colorant depending upon its chemical structure. Chemically similar colorants are given similar numbers eg. 77000 - 77996 are numbers of inorganic pigments.

One of 9 hues

"Colour Index"

C.I. Pigment Yellow 7

One of 19 application types   Identifying code

Types of synthetic organic pigment

The printing ink industry is by far the largest user of organic pigments, representing a usage of over 50% of the total production. There are various types of synthetic organic pigment.

Lakes (UK)

These are the oldest and now least used type of synthetic organic pigment. Some names are familiar to anyone associated with artists' colours – e.g. Crimson Lake, Madder Lake. These are made from natural dyes absorbed onto an absorbent inorganic base such as Kieselguhr or alumina hydrate. Following Perkin's discovery of Mauveine in 1856, countless new dyes became available and many of these could be used to make lakes. Such lakes are rarely used today except occasionally in inks and food dyes (Tartrazine lake etc.). Some of the last to survive are Quinizarin Lake (C.I. Pigment Violet 5), which uses Alumina as a base, and Pigment Scarlet 3B Lake (C.I. Pigment Red 60: 1), which uses aluminium hydroxide and zinc oxide as a base.

To confuse the issue the term "Lake" is widely used in the USA and elsewhere to describe compounds that are called "Toners" in the UK.

Toners (UK)

Toners are metal salts of dyes, mainly acid dyes in which the anion is the dye molecule and is the source of the colour. If the metal cation is lithium, potassium, sodium or ammonium then the colorant that is formed is soluble and therefore a dye. However, salts produced with metals such as calcium, manganese, barium, strontium etc, are mainly insoluble. This is an simple and economic method of producing pigments that find significant usage in printing inks.

C.I. Pigment Red 57:1 (Lithol â Rubine or Rubine Toner), is the most important example as it used as the standard magenta in four colour printing processes. However, there are more complex toners for use in the coloration of plastics, C.I. Pigment Yellow 183, Pigment Yellow 191 and Pigment Red 257 being good examples.

It is also possible to produce salts from basic dyes, the dye cation providing the coloured part of the molecule. Cationic dyes (or Basic dyes) are complexed with complex acids, such as phospho-tungstomolybdic acid. The BASF trade mark "Fanal" is often used to describe these pigments, which

are used to produce very strong, bright colours, but with poor fastness properties, limiting their use for packaging inks and poster paints.

Pure organic pigments

There is no generic name applied to the remaining class, the term "pure organic pigment" is used in this module. However, while most "pure" organic pigments are metal free, some may contain a metal group complexed into the molecule, such as copper phthalocyanine (C.I. Pigment Blue 15).

Differences between organic and inorganic pigments

As new products develop some of the traditional differences in characteristics that distinguished organic pigments from inorganic pigments are no longer valid. However as a rule of thumb, Table 2 can be used as a guide.

Table 2: Comparison between the properties of inorganic and organic types of pigment

	Inorganic	Organic
Derivation	Minerals	Synthesised from oil
Colour	Often dull	Bright
Tinctorial strength	Low	High
Opacity	Opaque	Transparent
Light fastness	Very good	Poor to very good
Solubility	Insoluble in solvents	May have some solubility
Physiological properties	May be problematic	Usually safe
Chemical stability	Often sensitive	Usually good (except Toners)
Cost	Often cheap	Can be expensive

It must be emphasised that this table is a generalisation. There are bright inorganic pigments and the tinctorial strength of organic pigments varies enormously. Certain forms of inorganic pigment are transparent and there are forms of organic pigment that have high opacity. The solubility of organic pigments varies from poor to excellent and their cost can vary from around £5 per kilo to well over £100.

Chemical structure and properties

Colour and constitution

The basic understanding for the relationship between chemical constitution (molecular structure) and colour was postulated by Witt in 1876, who also introduced the associated terminology.

A chromophore ("colour bringer") can be defined as an unsaturated functional group (contains double bond(s)) from which colour can be developed, usually by attaching aromatic rings to form a chromogen (with a conjugated system).

The colour can be developed further by shifting the absorption of light to another wavelength by the introduction of auxochromes (which are usually weakly basic groups, eg -OH, -NH_2, $N(CH_3)_2$) to the aryl rings.

An example of these structures is shown in (Figure 2). Biphenyl is colourless, but it does absorb radiation in the UV region of the electromagnetic spectrum.
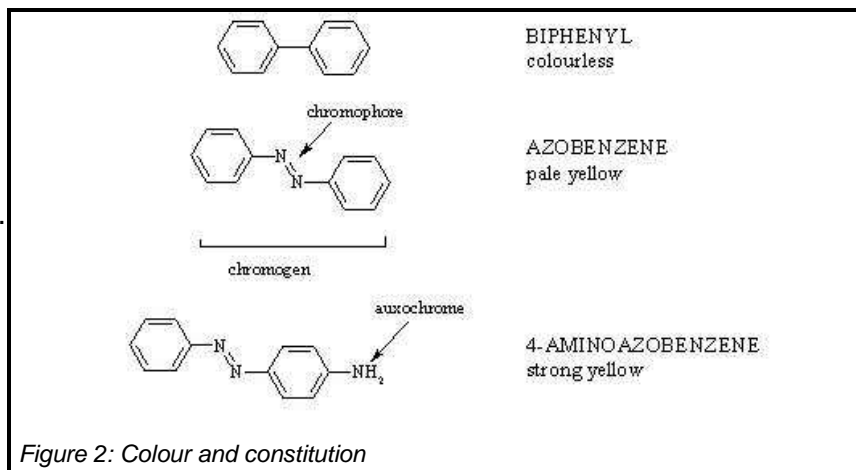

Figure 2: Colour and constitution

In biphenyl the two benzene rings are not conjugated, they cannot share / delocalise the bonding electrons between the two aromatic rings. By introducing an azo linkage into the molecule to form

azobenzene, the double bonds within the molecule become conjugated and there is a shift in the absorption wavelength (λ_{max}) to a longer wavelength (lower energy) of absorption. The molecule becomes coloured (pale yellow).

Increased conjugation in a molecule leads to a lower energy needed to promote an electron to a higher energy level, therefore, there is a shift of the wavelength of maximum absorption (λ_{max}, lambda$_{max}$) from the UV region into the visible region. Adding the auxochrome (NH_2) leads to the molecule becoming strongly yellow in colour.

Figure 3: Examples of common chemical classes of organic colorant
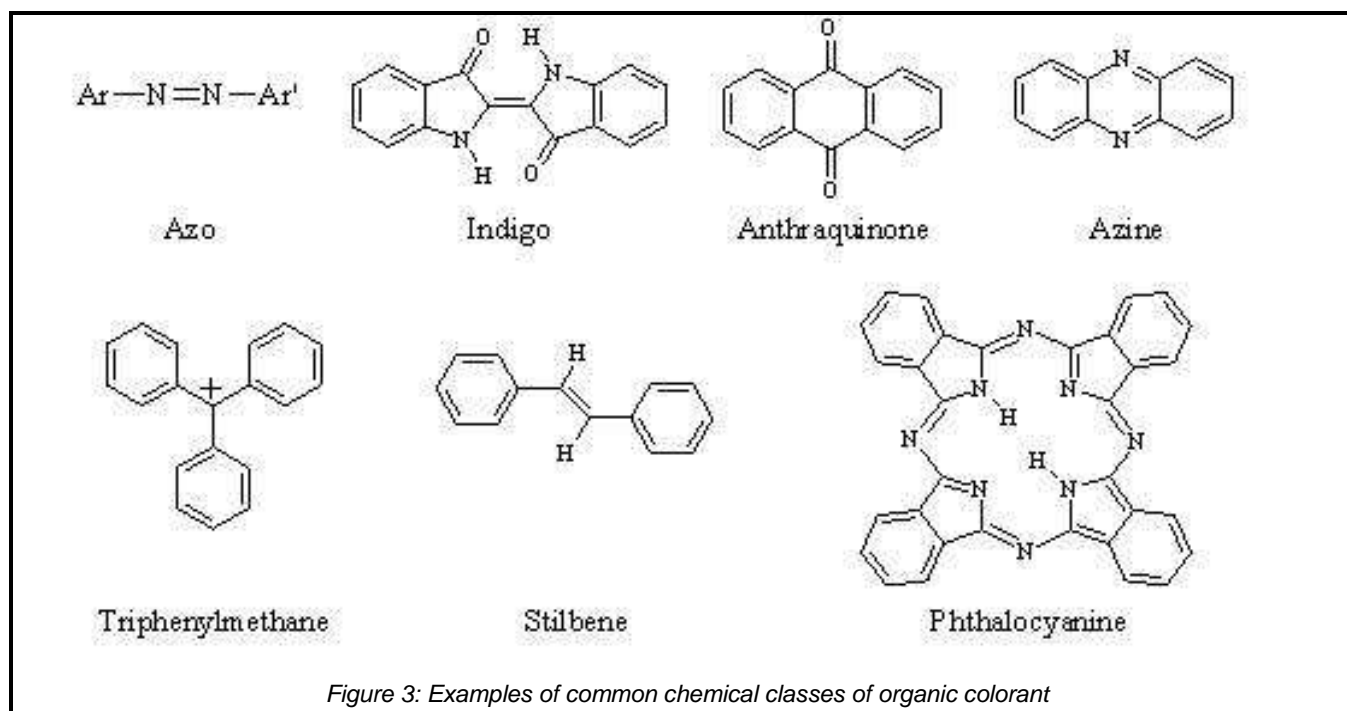
There is a range of chromophoric systems and these correlate to the chemical classes listed in the Colour Index. Examples of the chemical structures for some of the more important classes are displayed in Figure 3.

Structure and solubility

Although by definition pigments are insoluble, in practice they may have some solubility in organic solvents, especially at elevated temperatures. Solubility of the pigment can lead to a number of problems such as the staining of materials by bleeding and blooming.

Insolubility can be imparted into an organic molecule in a number of ways, however most of them increase costs.

Increasing molecular size decreases solubility, therefore in general the more complex the pigment, the better the resistance to solvents. However, just building up the size of the molecule is likely to have other effects, such as reducing tinting strength and increasing costs.

Adding certain substituents can either increase or decrease a pigment's insolubility. Long chain alkyls, alkoxy, alkylamino and acids such as sulphonic acids groups all increase solubility, whereas insolubilising groups include carbonamide (-CONH-), nitro and halogens. These groups have proved particularly effective for the so-called "Azo" pigments.

Introducing a metal group reduces solubility. The formation of metal salt with certain water-soluble dyes that contain carboxy acid or sulpho groups can make the colorant insoluble. The more acid groups in the dye, the better the solvent fastness obtained. This is a relatively cheap method, but usually reduces chemical stability

Intermolecular bonding between the molecules within the pigment particle can often result in pigments having much better resistance to solvents than one would expect from their molecular structure. The best example of such a pigment is linear trans quinacridone (C.I. Pigment Violet 19). If the shape of the crystal does not allow the formation of secondary intermolecular bonding, (i.e. the a crystal modification) the molecule does not have good resistance to solvents, whereas the b and g modifications have excellent solvent fastness.

The cost of organic pigments is usually related to their chemical structure. The more complex the molecule the more expensive the pigment. However, even in this respect there are exceptions and there is no better example than phthalocyanine pigments. This is a very complex molecule but is relatively easy to synthesise, making copper phthalocyanine among the cheapest of organic pigments.

Particle size, shape and structure

Particle size

Aside from the colour produced by a pigment, the most important physical property is the particle size because it affects nearly all other pigment properties (including colour). This important property is not easy to define and is usually characterised by the particle size distribution or the mean particle size. The shapes of the pigment particles are also important and must be considered in any instrumental assessment of particle size.

Inorganic pigments tend to have a mean particle size in the region of 0.1mm to 10mm. The characteristic properties are a moderate ability to add colour to a material (tinting strength), produce opaque colours that have a matt appearance, a good resistance to most chemicals and to solvents and excellent resistance to colour fading during prolonged exposure to light.

Organic pigments tend to have a particle size in the region of 0.01mm to 1mm. The characteristic properties are high tinting strength, produce transparent colours that have a glossy appearance and have poorer resistance properties compared to inorganic pigments.

The size of an individual pigment particle can be measured but this is not very useful except for determination of the primary particle size. A more useful indicator of particle size is to measure the distribution of sizes of the particles in a pigment sample and then calculate some average value. The term particle size must be used with care since there are a large number of different ways of measuring and calculating particle sizes. Generally the term particle size is taken to mean the diameter of the equivalent spherical particle that has the same property.

There are many methods of particle size analysis, with different properties of particles being measured; hence slightly different particle diameters are obtained, so care must be taken when comparing data. Generally the mean particle, mode particle size or the particle size distribution can be reported. The surface area of a pigment powder is an important size related property that has a direct influence on the flow properties of dispersions; the units of m^2 per gram of pigment are used.

Particle shape

Figure 4: Common particle shapes
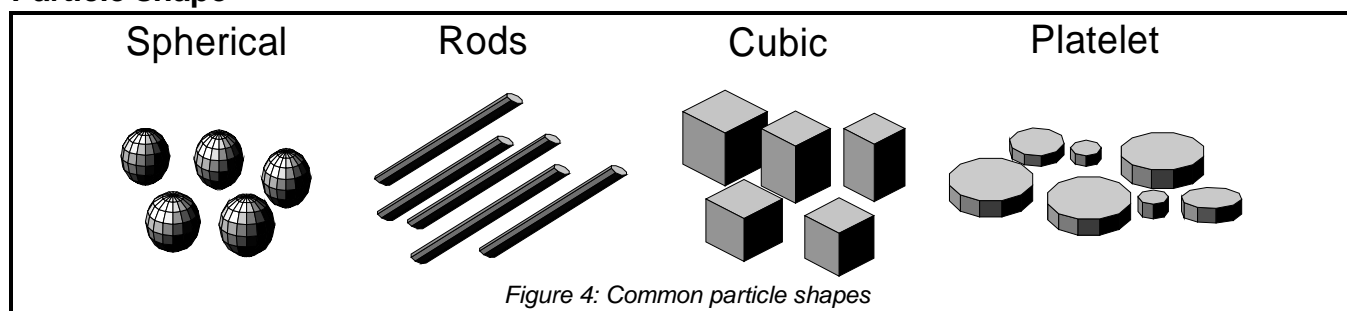
Since not all pigment particles are spherical or even regularly shaped a number of shape factors are used to aid determination of particle size, but these are often very complex. Some common particle shapes are illustrated in Figure 4, but many pigment particles simply have an irregular shape.

Crystal structure

Pigment particles can have one of a number of possible crystal forms. Each form may have different properties including light fastness and solubility. The most widely used pigment, titanium dioxide, has three crystal forms: anatase, rutile and Brookite, although only the anatase and the rutile forms find applications as pigments. The blue pigment copper phthalocyanine is known to have five different crystal modifications termed a, b, g, d and e. Not all of these modifications are suitable for use as a pigment due to unsuitable colour or handling properties.

Crystal modification may sometimes cause problems in a coating system if the particular pigment is prone to changing form. Recrystallisation is aided by small particle size, low solvent fastness and high temperatures, so care must be taken to choose a stable crystal modification for certain types of applications.

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