An Introduction to Pigments

The word “Pigment” is derived from Latin, “pingere” meaning to paint which gave us the noun “pigmentum” translated as paint or colour.

The word as used for coloration purposes is often confused with the same word used in biology to describe colours found in animals and plants, e.g., as in skin, eyes, flower petals, etc., which may or may not conform to our definition.

Definition:

The Color Pigment Manufacturers’ Association of North America (CPMA) have defined pigments as:

“*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*".

They are distinguished from dyes in that they are insoluble, and retain their insolubility throughout the coloration process, remaining particles. While most dyes are soluble, some are insoluble, but during the coloration process they are made soluble, by chemical reduction (Vat Dyes), elevated temperature (Disperse Dyes) or by incorporation into molten polymer at a very high temperature (Solvent Soluble Dyes). Sometimes such chemical constitutions can be either dyes or pigments, depending on the application process.

a) Inorganic or Organic.

Inorganic pigments have been used throughout history, as body paints for possibly 100,000 years, then as paints used to decorate cave walls in Asia (in Sulawesi, Indonesia, which are 45,500 years old), Europe (Chauvet, France, 29,000 years old) and Africa (Blombos, South Africa, alleged to be up to 70,000 years old).

The Egyptians introduced the first synthetic inorganic pigments when they roasted sand, copper containing minerals such as azurite or malachite, with a sodium containing mineral such as sodium carbonate at 800-900°C to produce a glass-like substance now called Egyptian Blue (calcium copper silicate), over 4,700 years ago. It is possible they learnt this technique from the Chinese even earlier.

Other inorganic pigments were obtained from the earth, consisting mainly of red and yellow ochre (e.g., C.I. Pigment Yellow 42, C.I. Pigment Red 101, Pigment Black 11, forms of iron oxide).

Later, other pigments were produced from
cinnabar or vermilion (C.I. Pigment Red 106 – a bright red),
lapis lazuli (bright blue) and
orpiment or realgar (C.I. Pigment Yellow 39 - yellow and orange, based on arsenic sulfide).

Inorganic pigments continue to play a critical role in coloration technology, especially because many have excellent light and heat stability, and can therefore be used to colour glass and polymers, even when processed at high temperatures. However, many of the earlier pigments are no longer commercially available or have at best a restricted use, due to their toxicity or environmental concerns.

Organic pigments have a shorter history. The first such pigments were derived from natural sources, usually plants, but occasionally animals. A purple blue colorant, Indigo, was mainly used as a vat dye, which needs to be reduced **to bring about**

water solubility and in which form it can be used to colour cellulose fabrics, especially denim, **whereas** in its insoluble form it can be used as a pigment, albeit lacking in light fastness.
Others need to be laked with alum or other inorganic materials, often with some chemical bonding, to form “Lakes” such as Madder (C.I. Pigment Red 83).

The first synthetic organic pigments were insoluble salts of acid (anionic) dyes, typically barium, calcium, manganese.

Lithol Red was the first such commercial product introduced in 1899 (C.I. Pigment Red 49), shortly followed by
Lithol Rubine (C.I. Pigment Red 57:1), which is still one of the most important organic pigments used today.

Later, a group of pigments was derived from basic (cationic dyes) using complex acids such as phospho-tungsto molybdic acid (e.g., C.I. Pigment Red 81, C.I. Pigment Blue 1, C.I. Pigment Violet 1) or
Copper Ferrocyanide (e.g., C.I. Pigment Red 169, C.I. Pigment Violet 27, C.I. Pigment Blue 62.

Both anionic and cationic toner pigments are still used today, especially for printing inks.

A group of organic colorants that were insoluble by their nature were first patented, in 1880, but as Azoic dyes that were produced by impregnating fabric (usually cotton) with an alkaline solution of ß-Naphthol then immersing the fabric in a diazotised amine, so the insoluble colorant was formed inside the fibre, offering excellent wash fastness. The process had to be carried out at low temperature to prevent decomposition of the diazotised amine, so they became known as ice colours.

In the early 20th Century, many of these colorants were recognised as pigments in their own right. Although most early pigments were as products for the textile industry, in 1928, phthalocyanine blue (C.I. Pigment Blue 15) was discovered, or rather re-discovered (it had been identified as early as 1907) but needed to be “conditioned” by surface treatment in order to make it into a dispersible commercial product.

b) Insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated.

The term insoluble is used in relation to the vehicle into which the pigment is incorporated. Organic pigments are essentially insoluble in water, but may show some slight solubility in organic solvents, generally increasing as one goes through the series aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, esters, and ketones. This slight solubility may have detrimental effects on the pigmented system, such as blooming, migration and bleeding in paint and ink, blooming and migration in plastics, and plate out on polymer processing equipment. Blooming may affect the coating or plastic article itself while migration may stain materials in which the coating or polymer comes into contact, especially foodstuffs, often making it quite unsuitable. Our ability to detect this staining is now much greater, and the requirements that the foodstuff is not stained have become even more demanding, so there is an ever-increasing demand for pigments with lower solubility.

Solubility also increases with temperature. Therefore, if heat is involved in incorporating the pigment into a vehicle, such as in processing polymers, the pigment may start to dissolve leading to technical problems, such as blooming or migration. Crystalline polymers such as polystyrene can often retain these dissolved pigments in their matrix, whereby the dissolved pigment is really a solvent soluble dye, whereas more amorphous polymers like polyethylene cannot prevent recrystallization limiting those colorants use in that polymer.

Likewise, if heat is involved after the pigment has been incorporated into a vehicle, such as heat-set inks or industrial stoving paints, this can cause the pigment to dissolve leading to blooming and appearing on the surface of the paint or ink.

One should also consider the long-term effect of the pigmented paint. While one may not experience any problems with slightly soluble pigments in a coloured paint, if one where to overcoat it with a white or pale coloured paint, the pigment may dissolve in this paint causing discoloration, a phenomenon known as bleeding, but it is not limited to red pigments.

c) They alter appearance by selective absorption and/or scattering of light.

In respect to their ability to selectively absorb and reflect wavelengths, pigments behave in a similar way to dyes but unlike most dyes, pigments also scatter light. This is a function of their refractive index, the greater the difference in the refractive index of the pigment from its binder, the greater its scattering power. Hence, the most important of all pigments (in terms of usage) is titanium dioxide, which is used not just to create a pure white, or to reduce the depth of coloured paints, but also to provide very high levels of opacity due to its ability to scatter light. Particle size can also affect the scattering power of a pigment.

A normally opaque pigment, even titanium dioxide (C.I. Pigment White 6), can be made transparent by reducing its particle size, thus reducing its ability to scatter light. However, the opposite is not true, while increasing the particle size does increase scatter, which is only up to a maximum particle size, which is approximately half the dominant wavelength of incident light, scattering then starts to reduce, with a subsequent reduction in opacity.

Some pigments which are transparent have a particle size larger than this maximum. This phenomenon is being termed (not strictly correctly) as “ultra-transparency”, but as it also leads to pigments with a very low tinctorial strength, it has limited application.

d) Pigments are usually dispersed in vehicles or substrates for application, as for instance in the manufacture of inks, paints, plastics, or other polymeric materials.

The technology around pigment using industries is about dispersing the pigment into a resin, binder or polymer. Before dispersion the pigment exists in either agglomerate (loosely bound clusters of particles) and aggregates (crystal particles joined along boundaries). The dispersion process breaks down the agglomerates into much smaller agglomerates and may even reduce them to primary particles, i.e., single crystals not adjoined to other crystals.

Traditionally, pigments were dispersed into oil with a mortar and pestle, a method still used by some artists. Modern dispersion techniques may involve bead mills, using beads made from very hard materials such as glass, ceramic or zirconium oxide. Bead mills are used extensively in both the paint and ink industries.
To incorporate pigments into polymers, the molten polymer provides high shear conditions using the screw of an extruder or injection moulding machine. It should be noted that if one uses too high a temperature the shear reduces and there is less shear generated. This temperature can vary depending on the polymer and the length of the screw.

In general, the smaller the pigment particle the more difficult it is to disperse. Many inorganic pigments will disperse relatively easily. Some of the fine organic pigments require some surface modification for adequately dispersing them, a process called conditioning or finishing. Many pigment users buy their pigments in a pre-dispersed form known as preparations or in plastics as masterbatch, offered either by the pigment manufacturer or by companies who specialise in this technology. The Colour Index lists many of these types of dispersions that are offered as single pigment colours.

e) Pigments retain a crystal or particulate structure throughout the coloration process.

It may appear strange that a pigment may also be a dye, depending on how it is processed. The best examples are Vat dyes. These are insoluble, but when used as a dye are reduced to their solubilised leuco compound and in this form applied to fibres by a dyeing process. Once in the fibre, the dye is oxidised back to its insoluble form, giving what is normally a very "wash-fast" coloration. Clearly these colorants have not retained their crystal or particular structure throughout the coloration process, so cannot be considered pigments (e.g., C.I .Vat Orange 7).

This is in contrast to textile printing where the crystalline form of the colorant is maintained throughout the process. When the same chemical compound (e.g., C.I. Pigment Orange 43) can be dispersed into a binder as a pigment. Usually, the surface of the vat dye has to be modified to enable the pigment to be dispersed, so many of these colorants existed as vat dyes long before a suitable conditioning process had been applied in order to allow them to be used as pigments.

The crystalline structure of a pigment is critical to its application properties. The same chemical entity very often exists in more than one crystalline form. Probably the best-known example is phthalocyanine blue (C.I. Pigment Blue 15).

The first phthalocyanine pigments to appear on the market were known as α-phthalocyanine, which are designated C.I. Pigment Blue 15. It had a reddish shade and good fastness properties, except when in aromatic solvents, which can convert the pigment to ß-phthalocyanine (C.I. Pigment Blue 15:3), a much greener and very stable pigment. The α-phthalocyanine form can be stabilised to prevent this transformation, by very slightly chlorinating it (approximately one chlorine atom per two phthalocyanine molecules). This so called stabilised α-phthalocyanine is designated C.I. Pigment Blue 15:1. Another crystal modification of phthalocyanine blue is ε-phthalocyanine, which is distinguished by its very pure red shade, and very high colour strength.

Another pigment which is very dependent on its crystal form is linear trans quinacridone, C.I. Pigment Violet 19. The α form is totally unsuitable as a pigment. Whereas the ß form is a reddish violet with excellent fastness properties. While still designated C.I. Pigment Violet 19, the γ form is a bluish red, and retains its high fastness properties.

If pigments dissolve during their dispersion or processing, they may recrystallise. This may very well be in a different crystal modification, which may lead to a change in the pigment's application properties. As this recrystallisation may take place over a period of time, the result is a very unstable system, and must be avoided.

Chemical Constitution

The details of the chemical constitution (structure) must be revealed to the Society of Dyers and Colourists before it can be registered in the Colour Index, although this constitution is not published if requested by the registrant that it be held in confidence and it is not in the public domain. Although in some cases data mining by Chemical Abstracts has removed the confidentiality of the structure as it was disclosed in chemical registrations, patents or literature articles.

A few pigments still remain with undisclosed structures that were registered before this condition was made mandatory. Historically, there are a few inconsistencies depending upon how particular crystalline pigments were registered and assigned colour numbers by Colour Index committees.

Better understanding of structures (including post-treatments) has made listings much more consistent.

a) Organic pigments

Terminology used for organic pigments can be confusing.

The majority of such products do not contain any salt forming groups, they are simply known as “organic pigments” and can be further classified according to their constitution.

The largest group is azo, subdivided into monoazo and disazo and cover the yellow, orange, red and a few violets and a single blue pigment. These azo pigments can provide higher fastness properties by enlarging the molecule by the addition of benzimidazolone and by condensing two molecules together with a diamine to produce disazocondensation pigments.

In the blue and green hue range copper phthalocyanine pigments predominate, (e.g., C.I. Pigment Blue 15, C.I. Pigment Green 7). Indanthrone Blue (C.I. Pigment Blue 60) does have a niche position in the market due to its unique shade.

Important subgroups in the yellow/orange parts of the spectrum include:
isoindolinone
isoindoline
anthrapyrimidine
flavanthrone
diketo-pyrrolo pyrrole (DPP) and
perinone

In the red part of the spectrum azo pigments are supplemented by
perylene
quinacridone
anthraquinone
thioindigo and
diketo-pyrrolo pyrrole (DPP)

The violet sector is dominated by dioxazine violets and there is a red-blue shade Indanthrone violet.

There are some brown and black organic pigments for speciality applications, such as metallic paints, IR reflective finishes for camouflage and heat reflecting finishes.

b) Toners

In the UK and a few countries that follow their convention, Toners are pigments formed by reacting a water-soluble dye with a metal containing compound. Barium, calcium, manganese, magnesium salts are prepared using azo acid dyes.

They are mainly used for inks, especially C.I. Pigment Red 57:1, which is the most common pigment used to provide the magenta ink used as the standard in three and four colour inks.

It is more difficult to precipitate basic dyes, but a series of toner pigments is manufactured using very bright basic dyes (mainly aryl carbonium compounds) with complex heteropoly acids such as phosphotungsto molybdic acid (e.g., C.I. Pigment Red 81) or copper ferrocyanide (C.I. Pigment Blue 62). These pigments are usually limited to printing inks.

In most countries such pigments are known as lakes and just to confuse matters, the term “Toner” is sometimes used in the USA to describe organic pigments. Also the term is now widely used for the products used in laser printers and photocopiers.

c) Lakes

Lake pigments were originally made by absorbing water-soluble dyes (often from natural sources) onto an absorbent base, such as blanc fixe, kieselguhr or alum, although alum can also form so weak bonds with the dye.

Dyes used include azo compounds and anthraquinone. Because the base onto which the dye is absorbed is uncoloured, such pigments have low tinctorial strength and their use has substantially reduced, but they are still used in food lakes and cosmetics.

d) Inorganic Pigments

As previously mentioned, the history of inorganic pigments goes back millennia and the ochre (iron oxide) pigments are still widely used in paints, due to their economic price and good fastness properties that make them a popular choice from pale autumnal shades in decorative paints, to highly transparent grades for automotive metallic and pearl finishes.

There are many new man-made compounds, with very high heat stability and excellent light fastness, known as complex inorganic-coloured pigments (CICP). CICPs are typically crystals of mixed metal oxides that are produced by a high temperature calcination process. They have a defined crystal structure (e.g., rutile and spinel). One CICP can have a variable ratio of metals to provide the desired colour to the pigment. Particular CICPs are allowed specific modifiers (compounds such as metal oxides, or elements) added at low levels that adjust the pigment tint without altering the crystal structure. A mineralizer may be added in the calcination process to modify pigment formation by facilitating crystal growth. The heat stability of these CICPs makes them very useful for the coloration of polymers, including many engineering polymers, ceramics and glass.

Bismuth vanadate (C.I. Pigment Yellow 184) is a brilliant yellow inorganic pigment with good heat and light fastness properties. This inorganic pigment can be produced by high temperature calcination of bismuth and vanadium oxides, thus making it a CICP. It can also be produced by carefully pH-controlled precipitations. Applications include inks, plastics and coatings.

Ultramarine (C.I. Pigment Blue 29) is a bright blue inorganic pigment with excellent light and weathering fastness. It is composed of sodium aluminium sulphosilicate with a structure similar to a zeolite. Synthetic Ultramarine is much less expensive than the naturally occurring mineral lapus lazuli. Ultramarine is used in a variety of applications, including coatings, and food and cosmetic packaging.

Included in the inorganic pigment classification are several white pigments that absorb visible wavelengths of light, rather than reflect them (or at least most of them). Many of the inorganic pigments used over the centuries (including some white pigments) have declined in use because of concerns about their toxicity or ecotox properties. These include compounds of lead, cadmium, chrome, mercury, and arsenic. Most white pigments have been replaced by titanium dioxide (C.I. Pigment White 6), which can have a mostly rutile or anatase crystal structure. Because of its excellent opacity and good properties, titanium dioxide is almost universally used as the white pigment of choice, in printing inks, paints, plastics, packaging and cosmetics.

Finally, there are some inorganic pigments that have application as anti-corrosive products, although their use as declined mainly on concerns about their toxicological properties. Zinc chromate (C.I. Pigment Yellow 36) was particularly effective in protecting iron and aluminium, but as it reacts with the substrate (much as a paint primer), so it does not strictly conform to our definition of a pigment. Lead chromate (C.I. Pigment Green 15) was used in paints and other applications but is now restricted due to its toxicity.

e) Extender pigments

Although they do not always quite fit the definition we have given, many extender pigments are included in the Colour Index. Their main use is to control the rheology of coatings, reduce the gloss by acting as a matting agent, or improving durability or adjusting for the strength differences between production lots.

Chalk (C.I. Pigment White 18), China Clay (C.I. Pigment White 19), Talc (C.I. Pigment White 26) and Barytes (C.I. Pigment White 22) are among the most common extenders used, with silica being a popular matting agent. Most have a natural source and even after purification tend to be inexpensive and easy to disperse. They do not have a special place in the Colour Index but are included within other pigments of the metal group to which they belong.

f) Metal Pigments

A very small group of pigments, mainly simple metal pigments that can be used in coatings to provide a metal effect.

Aluminium powder (C.I. Pigment Metal 1) is the most important, being used for striking metal flake paint finishes, frequently seen on cars, motorcycles and bicycles. They are occasionally mixed with basic dyes to provide brilliant colours.

Zinc powder (C.I. Pigment Metal 6) is used to enhance metal protection and bronze powder (C.I. Pigment Metal 2 - based on copper) is used in decorative inks and some security inks.

g) Carbon Black

One pigment group that has characteristics of both organic and inorganic pigments is Carbon Black (C.I. Pigment Black 6 and Black 7).

There are many grades of carbon black, usually produced by incomplete combustion of hydrocarbons such as natural gas and oils, rather than organic synthesis. The resulting carbon black substances are mainly carbon, typically very small particles with differing morphologies, which behave much more like organic pigments than most inorganic pigments. Nevertheless, it has been given a Constitution Number (CICN) 77266, which is in the middle of the inorganic section.

Fastness Properties

In earlier editions of the Colour Index many of pigments were given fastness data such as light fastness, fastness to solvents, heat stability and chemical resistance.

In discussions with pigment manufacturers the inconsistencies of such classification became clear. Light fastness depends not only on the pigment but on the protection provided by the binder. Thus, the same pigment would have quite different light fastness depending on whether it was used in a printing ink (where it would be given little protection from the binder) or in a paint (water-based emulsion or latex binder give less protection than acrylic/melamine stoving paints). The best protection is given by polymers.

Particle size also has a profound effect. In recent years large particle size pigments have been introduced, mainly to improve opacity. However, a side effect is that large particle size pigments have significantly higher light fastness than the finer particle size grades. In the case of C.I. Pigment Orange 34, the difference is between 2 and 3 points on the Blue Wool Scale, or a factor of 6!

It was suggested that each manufacturer could give data relating to their product. This was strongly opposed by pigment manufacturers as putting such comparative data in one source, would tempt manufacturers to exaggerate their products fastness, especially as no standard tests are universally accepted. It is recommended that before selecting a pigment, one should always test it in accordance with their requirements and not to assume that chemically identical pigments will give the same fastness properties.

Approved Oct 2022 SDC CIPSDTB
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