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The Chemical History of a Paint Box

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Abstract: The history of mankind is the history of colour. The colours of objects, fabrics, manuscripts and illustrations from the past betray their cultural origins. A look into the modern paint box reveals some of the chemical history associated with colour.

Keywords: Chemistry · Colour · History · Paint · Pigment

Humans see the world in colour. Our perceptions and representations of our environment and cultural identifications are polychromic. Nowhere is this better illustrated than in the artistic creations of mankind. Painting is one of the foremost ways we convey our perception of the world – whether naturalistic, impressionist, representational or entirely abstract, our art relies upon tools to modify a base medium.[1] One of the most familiar of these tools is the paint box. This article examines the wealth of chemistry in that simple paint box (Fig. 1)!

Fig. 1. A typical selection of oil paints (Photo credit, Edwin C. Constable).

Paints typically consist of pigments suspended in a liquid. This article considers oil paints, where the liquid is an oil such as linseed oil, which hardens as it oxidises in the air. Pigments are coloured materials which are insoluble in the chosen liquid. Both inorganic and organic pigments are encountered today, although the introduction of synthetic organic pigments dates back to the 19th century.[2] Often, the inorganic materials have greater longevity and higher light stability, whereas the organic pigments are usually less toxic. Finally, because the colour we observe is scattered from pigment particles, we see the complementary colour to that absorbed (Fig. 2). If a pigment absorbs yellow light, the reflected light that we observe will result in a purple or violet appearance.

What might be in our paint box? It is likely to contain several yellow paints such as Cadmium Yellow, Yellow Ochre or Hansa Yellow. Before, considering these, it is worth looking back to the

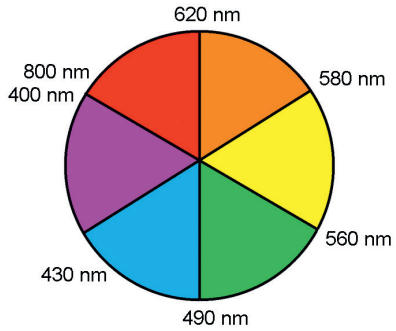

Fig. 2. A colour wheel. If a colour is absorbed, the observer sees the complementary colour diametrically opposite on the colour wheel. Image created by Tem5psu, https://commons.wikimedia.org/wiki/File:Colorwheel_wavelengths.png.

historical palette. This might have contained Yellow Ochre, but also Naples Yellow ($Pb_2Sb_2O_7$), orpiment or gamboge (As_2S_3), both of which were highly toxic. By the 19th century, these were generally replaced by the modern pigments and by Chrome Yellow ($PbCrO_4$), the latter being equally toxic. Yellow Ochre is a hydrated iron oxide of approximate formula $FeO(OH)\times nH_2O$ which is cheap and readily available. The colour is an earthy yellow-brown and it does not have the brightness of pigments such as Lead Chromate or orpiment. Typically, the yellow ochres have broad absorptions with an onset close to 535 nm and running into the near IR region, primarily due to ligand-to-metal charge transfer transitions. Cadmium Yellow is cadmium sulfide and, although cadmium is toxic, it is still widely used as a pigment in paints. Cadmium sulfide is a semiconductor with a band-gap of 2.42 eV (512 nm) and the colour is due to absorption of light in the blue-green region of the spectrum. Although the majority of historical and modern pigments are relatively simple inorganic materials, the Hansa Yellows are representatives of a class of synthetic organic materials designed to be less toxic. These are known as azo dyes, and a generic structure is presented in Fig. 3.

The tubes of red paint are likely to include Vermillion and Carmine Red. Traditionally, Vermillion was α-HgS, but today the paint is as likely to contain $CdS{\cdot}nCdSe$ which was introduced to avoid the toxicity of mercury compounds. It is debatable whether the cadmium substitutes are significantly safer. HgS is a semiconductor with a band gap of 2.3 eV (540 nm). Other traditional red pigments including Venetian Red and Indian Red are based on various forms of iron(III) oxide. Important historical pigments included realgar (As_4S_4) and minium or red lead (Pb_3O_4), both of which have toxicity hazards associated with them. Minium was an early example of a synthetic pigment, being prepared by heating lead(II) oxide in air. The name derives from the river Miño in Spain. Although we think of organic pigments as being a modern discovery, the pigment carmine (Fig. 4a) has been known since antiquity. Carmine is an aluminium complex of carminic acid, which is extracted from cochineal beetles (*Dactylopius coccus*) and has been used as a dye and pigment since antiquity. Alizarin (Fig. 4b) has a similar heritage and was extracted from madder until it became the first natural pigment

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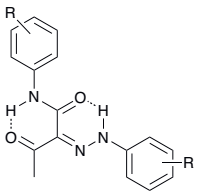

Fig. 3. A generic structure of an azo dye such as one of the Hansa Yellows. Hydrogen bonds are shown by dotted lines.

to be prepared by synthesis in 1869. Numerous synthetic red-purple pigments based on quinacridone (Fig. 4c) are now used in oil paints. All of these organic materials exhibit extended conjugated structures, and the colour arises from $\pi^* \leftarrow \pi$ transitions.

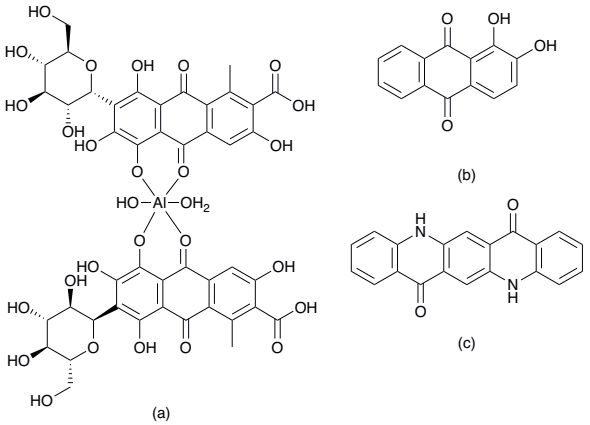

Fig. 4. The structures of some red organic pigments or precursors, (a) carmine. (b) alizarin, and (c) quinacridone.

Green pigments have had a chequered history. Modern paints include Emerald Green and Chrome Green but the journey to these was sometimes tortuous. Emerald Green, also called Vienna Green, Schweinfurt Green, Paris Green or Scheele's Green, was a synthetic copper arsenite of idealised formula $CuAsO_3$ first introduced in 1814 and which proved to be immensely popular with the 19th century artists and general public. It was extremely toxic, being blamed for the death of Napoleon, and was banned by the beginning of the 20th century. Today the paints labelled Emerald Green usually contain phthalocyanines, most often chlorinated copper phthalocyanine (Fig. 5, X = 1–16 Cl). Variations on the name Chrome Green or Viridian are associated with paints containing Cr_2O_3 as a pigment and are still utilised today. The oxide is a semiconductor with a band-gap of ≈ 3 eV (≈ 410 nm). Cobalt (or Rinman's) Green is a synthetic material, $CoZnO_2$, still found in modern green paints although it is generally inferior to the Chrome Greens. Historically, the earliest pigments were probably based on the copper mineral malachite, ($Cu_2CO_3(OH)_2$), which continued to be used through the 15th and 16th centuries.

And what of the blues? Many paint boxes will have Prussian Blue, Ultramarine or Cobalt Blue. Each of these names represents their chemical heritage. In 1704, Diesbach accidentally prepared a blue pigment, which became known as Prussian Blue or Berlin Blue.[3] Blue pigments were rare and expensive, and the new colour was commercialised with the first painting (The Entombment of Christ by Pieter van der Wer) dated to 1709. Although Diesbach did not reveal how he made the pigment, a French recipe was published in 1724 and the compound was sold as Paris Blue. The compound is readily prepared today as a deep blue precipitate obtained in the reaction of iron(II) salts with $K_3[Fe(CN)_6]$ in aqueous conditions. The crystal structure of Prussian Blue ($Fe_4[Fe(CN)_6]_3 \cdot xH_2O$) was only determined in 1977. Some 12 million kilograms of Prussian Blue are prepared annually, mainly for use in inks. The blue colour is due to charge transfer between iron(II) and iron(III) centres and is associated with an absorption around 680 nm. Previously, artists relied on ultramarine, an intensely blue and expensive pigment obtained by grinding the mineral lapis lazuli. This is a complex mixture of minerals, with the dominant blue species having the variable constitution $(Na,Ca)_8(AlSiO_4)_6(S,SO_4,Cl)_{1-2}$. Since the late 18th century, ultramarine pigments have used a synthetic material, $Na_{8-10}(AlSiO_4)_6S_{2-4}$. The blue colour is associated with the presence of the $S_3^{\bullet-}$ radical anion, which has an absorption maximum of 595–620 nm. And why is it called ultramarine? This comes from the Latin *ultramarinus*, indicating that the material was imported by sea from the Middle and Far East in historical times. The third of our triad is Cobalt Blue. This primarily synthetic material is obtained by heating cobalt salts and aluminium oxide and possesses an ideal formula $Co(AlO_4)_2$ and a spinel structure. The colour is often lighter and less intense than ultramarine or Prussian Blue and the pigment is valued for depicting skies. The colour is due to absorption at 600 nm assigned to the $^4T_1(^4P) \leftarrow {}^4A_2(^4F)$ transition of tetrahedral cobalt(II). Finally, I should mention the intensely blue pigment, copper phthalocyanine, (Fig. 5, X = H) which is widely used in paints and numerous other applications.

We often ignore black and white as colours, but they are central to the artist's palette. Black pigments are of two common types. The first dates back to using charcoal for drawing and is based on finely powdered carbon from various sources. Names such as Bone Black, Lamp Black or Ivory Black betray their historical origins, although modern formulations are more sustainable. The second type of black pigment is based on metal oxides, typically forms of iron oxide, although more expensive manganese oxides have been used in the past. Mars Black and Iron Black are both forms of magnetite, Fe_3O_4, which adopts a spinel structure and contains iron(II) and iron(III) centres. The black colour is due to broad absorption across the optical spectrum. Modern Ivory Black often contains mixtures of carbon and magnetite, resulting in a slightly gentler colour. Historically, the most common white paints were based upon Lead White, a basic lead carbonate with an ideal formula $(PbCO_3)_2 \cdot Pb(OH)_2$. By the 19th century, lead-based paints were becoming a concern. On the one hand, the toxicity of lead was becoming fully appreciated. On the other, the pollution associated with the Industrial Revolution resulted in hydrogen sulfide in the air, which reacted with the pigment to form black PbS. Initial replacements in the palette included Zinc White (ZnO) and Lithopone (ZnS and $BaSO_4$), but most white pigments today are based on TiO_2, usually sold as Titanium White.

The paint box (Fig. 1) contains clues to the historical origins of the colours contained therein, but also provides a useful revision of the ways in which colours may arise in materials.

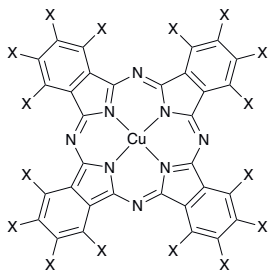

Fig. 5. The copper phthalocyanine structure that is ubiquitous in modern green and blue pigments.

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