PAINTS AND PIGMENTS

Paints have been manufactured since prehistoric times, but until recently they were highly expensive and thus were mainly used for artwork. It is only since the nineteenth century that houses have commonly been painted. Today paints are used for colouring and protecting many surfaces, including houses, cars, road markings and underground storage vessels. Each of these different applications requires a different sort of paint, and it is these differences in composition that are the focus of this article. Paint is essentially composed of a binder, pigment and solvent.

**Binders**
The binder exists to hold the pigment to the surface. The binder is a polymeric substance, and is either dissolved in the paint or suspended in it by emulsifiers.

*Drying oils*
These were used until the 1960's, and are natural oils that polymerise as they dry. They take a long time to dry and have variable properties as the balance of oils varies from crop to crop.

*Alkyd resins*
Alkyd resins are the most common resins to be used in solvent-based paints. They are basically polyesters and are used for both air-drying and heat-cured paints.

*Vinyl and acrylic emulsions*
These are emulsions in water and are the most common water-based binders for use in household paint.

*Epoxy resins*
These resins are based on polymers containing the simple organic compound 'oxirane' (ethylene oxide). A variety of other components are added to give a wide range of properties.

*Polyurethanes*
Polyurethanes are polymers of any ester of carbamic acid, H₂N—CO₂H. Polyurethane-based paints are tough, durable films that retain their gloss and are easy to clean. They are often used for painting aircraft.

**Pigments**
These not only give the paint its colour and finish, but also serve to protect the surface underneath from corrosion and weathering as well as helping to hold the paint together. Both inorganic and organic substances are used, with the inorganic ones being in general cheaper but with less clear colours. Special pigments can be used to give metallic finishes (for example for car bodies), to be hard wearing (for road markings) etc.

**Solvent**
A solvent must be chosen that dries evenly, and in which the binder is soluble but not so soluble that it won't polymerise. For emulsion paints the solvent is simply water, and for resin-based paints a variety of organic compounds are used with the most common being mineral turpentine.
INTRODUCTION

Paint is one of the oldest synthetic substances known, with a history stretching back into prehistoric times. It was made more than 35,000 years ago by prehistoric man as they mixed clays and chalks with animal fats and used these paints to depict their hunts on cave walls. By 2500 BC the Egyptians had improved this technology considerably. They had developed a clear blue pigment by grinding azurite, and instead of animal fats they used gums, wax and maybe also albumen (egg white) as binders and solvents for their paints. The technology improved still further during the first millennium BC as the Greeks learnt to blend paints with hot wax, rather than water, making a paint that was both thicker and easier to spread and thus making it possible to blend colours. By this time many colours were available from both natural and synthetic sources, one of the most interesting being a purple pigment made from heating yellow earth till it turned red and then plunging it into vinegar.

The technology then lapsed for many years, with techniques being passed down from generation to generation by travelling craftsmen. This continued until the eighteenth century, when paint factories began to be opened in Europe and America, and by the nineteenth century this mass production had brought prices down to such an extent that houses began to be painted. Now, in the twentieth century, the chemistry of many aspects of paint manufacture and function is understood, meaning that paint manufacture has finally moved from being an art to being a science.

Types of paint

The paint with which most people are familiar is the household paint. The modern household presents a wide range of conditions which the paint must protect against. The bathroom and kitchen are moist, warm areas which may promote the growth of mould. The living area needs to be bright, comfortable and, where young children or pets are around, easily cleaned. On the exterior, masonry presents different problems to those posed by the spouting: the roof has different problems to those posed by weatherboards. Paints are made for all of these situations as well as other paints for cars, lane markings on roads and for the protection of ships, underground storage vessels etc. All of these paints are essentially a mixture of a solvent, a binder (that sticks to the surface) and a pigment (which provides colour, opacity and protection of the surface concerned).

Modern household paints fall into two broad categories:

- Orthodox, oil-based paints, thinned with mineral turpentine or other organic solvents
- Emulsion paints, which may be vinyl or acrylic based and which are thinned with water

Until fairly recently, it was generally thought that, for applications such as painting external joinery, orthodox finishes were superior and for masonry etc., water thinnable paints were most suitable, but recent advances have blurred this distinction in properties. In many cases, it is now difficult to choose between oil based or emulsion paints in terms of properties.
MANUFACTURE OF PAINTS

The manufacture of paint is, in principle, fairly simple. The pigment, binder and thinner must be blended in the correct proportions such that, when the paint is applied, the final finished film is continuous, smooth and attractive to the eye.

The correct properties are achieved by the joint skills of the paint technologist who formulates the paint to meet certain predetermined standards, and the paint technician who manufactures the paint and ensures that the properties set down by the paint technologist are achieved.

The machinery used to manufacture paint are the province of the chemical engineer, who designs equipment which yields the results required by the paint technologist. Extensive detail of this type of equipment is outside the scope of this article, but the machinery in commonest use would be ball or pebble mills, horizontal and vertical bead mills and high speed intensive stirrers. For high quality finishes, triple or single roll mills are sometimes used, and there are many other varieties of machine available to the paint manufacturer.

In the laboratory the small scale ball mill, bead mill and small scale high speed mixer are commonly used.

THE COMPOSITION OF PAINT

Paint is essentially a mixture of a binder, which sticks the paint to the surface, pigments, to give the paint colour, make it opaque and occasionally to prevent corrosion and solvents to make the paint spreadable. The chemistry of these components is outlined below.

Binders

Paint technology advanced very little until this century. Even as recently as the 1960s 'drying oils' were the commonest paint binders. Drying oils are substances that, when spread out in a film, will dry to form a continuous skin. Linseed oil, the most common example of a drying oil, will dry in 2 to 3 days while other oils, such as soya bean oil, may take up to 10 days.

Linseed oil is a mixture of triglycerides of long chain carboxylic acids. Some of the major component carboxylic acids are:

- Linolenic acid
  \[
  \text{CH}_3\text{CH}_2\text{CH}==\text{CHCH}_2\text{CH}==\text{CH(CH}_2)_7\text{C}==\text{O} \quad \text{OH}
  \]
  \((\text{cis, cis, cis-9, 12, 15-octadecatrienoic acid C}_{18}\text{H}_{30}\text{O}_2)\)

- Linoleic acid
  \[
  \text{CH}_3(\text{CH}_2)_4\text{CH}==\text{CHCH}_2\text{CH}==\text{CH(CH}_2)_7\text{C}==\text{O} \quad \text{OH}
  \]
  \((\text{cis, cis-9, 12-octadienoic acid C}_{18}\text{H}_{32}\text{O}_2)\)

- Oleic acid
  \[
  \text{CH}_3(\text{CH}_2)_7\text{CH}==\text{CH(CH}_2)_7\text{C}==\text{O} \quad \text{OH}
  \]
  \((\text{cis, -9-octadecenoic acid C}_{18}\text{H}_{24}\text{O}_2)\)
Many common drying oils contain these compounds and others, including eleostearic and recinoleic acids, in various ratios.

The drying process is a complex one of polymerisation, probably catalysed by peroxides as described by Farmer in 1912. The theory is that drying progresses as follows:

1. double bonds are oxidised by atmospheric oxygen to give hydroperoxy groups:

   \[
   \text{CH}_2=\text{CH} + \text{O}_2 \rightarrow \text{CH}–\text{CH} \quad \text{OOH}
   \]

2. these peroxides then decompose to give radicals:

   \[
   \text{RO}–\text{OH} \rightarrow \text{RO'} + \cdot\text{OH}
   \]

3. the radicals then initiate various polymerisation reactions:

   \[
   \text{RH} + \cdot\text{OH} \rightarrow \text{R} + \text{H}_2\text{O}
   \]

   \[
   \text{R} + \text{O}_2 \rightarrow \text{RO'O}
   \]

   \[
   \text{H–C–O–O–H} \rightarrow \text{H–O} + \text{H–C–O'} \rightarrow \text{H}_2\text{O} + \text{C}=\text{O}
   \]

4. before recombining:

   \[
   \text{R} + \cdot\text{R} \rightarrow \text{R–R}
   \]

   \[
   \text{R} + \text{RO'} \rightarrow \text{R–O–R}
   \]

   \[
   \cdot\text{R} + \text{RO'O} \rightarrow \text{ROOR}
   \]

Other reactions also occur, including the Diels-Alder reaction:
The drying process may be accelerated by the addition of small quantities of metals such as lead, cobalt or manganese compounds. These are 'driers'. Lead compounds are rarely used in modern paints due to their high toxicity. Driers catalyse peroxide decomposition as follows:

\[
\text{ROOH} + \text{Co}^{3+} \rightarrow \text{ROO}^* + \text{H}^+ + \text{Co}^{2+}
\]

Natural compounds vary widely and the proportions of the constituent triglycerides will vary from batch to batch of oil. Various processes have been used to improve the properties of oils and, until the advent of modern technology, these processes all involved increasing the molecular weight of the oil by controlled oxidation.

**Alkyd resins**

The most important and extensively used solvent-based resins in the paint industry today are the alkyd resins (see article). They are classed as polyesters because the large resin molecules are built up by a process of esterification reactions.

An ester is produced by heating together an alcohol and acid:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{C}^\text{O} \rightarrow \text{CH}_3\text{C}^\text{O} + \text{H}_2\text{O}
\]

- ethanol (acetic acid)
- ethanoic acid (ethyl acetate)

Esters formed in this type of reaction from monofunctional constituents are chemicals of fixed, known and easily determined molecular mass and structure. They are non-resinous (many natural and artificial flavours are esters).

If polyfunctional ingredients are used, more complicated reactions occur:

\[
2\text{CH}_2\text{CH}_2\text{OH} + 2\text{HO}-\text{C}-(\text{CH}_2)_4-\text{C}-\text{OH} \rightarrow 2\text{CH}_2\text{CHCH}_2-\text{O}-(\text{CH}_2)_4-\text{C}-\text{OH} + 2\text{H}_2\text{O}
\]

- propylene glycol
- adipic acid
- half ester
- polyester

This type of reaction is carried out at temperatures of 180-250°C, usually under an inert gas blanket, until the required acid value or, alternatively, the required viscosity is reached.
The commonest starting products for the class of polyester resins known as alkyd resins are 1,2,3-trihydroxypropane (glycerol) and phthalic anhydride.

\[
\begin{align*}
\text{CH}_2\text{-OH} & \quad \text{CH}\quad \text{CH}_2\text{-OH} \\
\text{CH-OH} & \quad \text{O} \\
\text{CH}_2\text{-OH} & \quad \text{O}
\end{align*}
\]

glycerol \quad \text{phthalic anhydride}

A portion of the complex glycerylphthalate resin would look as follows:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\text{CH}_2\text{CHCH}_2\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{C} \\
\text{O} & \quad \text{O}
\end{align*}
\]

Other common components of alkyd resins are given in Table 1. However, alkyd resins made from the acids and alcohols alone are of little practical use in the manufacture of paints. Films formed from them are yielding, dull, soft, tacky films of poor durability. By incorporating oils in the reaction mixture some of the long chain carboxylic acids in the triglyceride are replaced by difunctional acids. This gives resins which yield films with good durability, excellent colour retention and superior gloss to films formed from drying oils alone. These are known as oil modified alkyd resins. Other agents that have been used to modify alkyds for use in paints are given in Table 2.

Many modern "oil-based" paints are alkyds modified in some way or other. Alkyds are used in both air drying paints and heat cured "stoving enamels".

A typical alkyd resin for use in glossy household paint would contain something similar to the following: 85 glycerol : 135 phthalic anhydride : 150 linseed oil : 135 abietic acid : 35 phenolic resins.
Table 1 - Alcohols and acids used in the manufacture of alkyd resins

<table>
<thead>
<tr>
<th>Polyhydric alcohols</th>
<th>Dibasic acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCH$_2$CH$_2$OH</td>
<td>![Dibasic acid structure]</td>
</tr>
<tr>
<td>HO—(CH$_2$)$_n$—OH</td>
<td>![Dibasic acid structure]</td>
</tr>
<tr>
<td>HO—CH$_2$CH—CH—CH—CH—CH—CH$_2$—OH</td>
<td>![Dibasic acid structure]</td>
</tr>
<tr>
<td>CH$_2$OH</td>
<td>HO—C—(CH$_2$)$_8$—C—OH</td>
</tr>
<tr>
<td>HOCH$_2$—C—CH$_2$OH</td>
<td>![Dibasic acid structure]</td>
</tr>
<tr>
<td>CH$_2$OH</td>
<td>![Dibasic acid structure]</td>
</tr>
</tbody>
</table>

Emulsions
Alkyd paints consist of a pigment, solvent and binder which are all mutually soluble. An emulsion paint, on the other hand, consists of pigment and solid or semi-solid polymeric particles dispersed in a continuous aqueous medium in which they are insoluble. This emulsion is made from monomers, initiators (which cause the monomers to polymerise and act as the binder), water and emulsifiers (which keep the monomers and later the polymers in the emulsion). Water-based paints based on acrylic and/or vinyl emulsions are the most extensively used paints in the retail decorative market, accounting for some 70% of the volume.
### Table 2 - Additives used in alkyd resins

<table>
<thead>
<tr>
<th>Additive</th>
<th>Function</th>
</tr>
</thead>
</table>
| ![molecule](CH=CH2) | • Reduce drying time  
• Improve durability of paint |
| ![molecule](CH=CH2-CH3) | • Reduce drying time  
• Improve durability of paint |
| ![molecule](Si-O-Si) where R is commonly methyl (CH3) or ![molecule](CH3) | • Co-polymerise to make more durable glossy paints  
• Especially effective with dark paints |
| ![molecule](abietic-acid) abietic acid (rosin) | • Dries quickly  
• Produces glossy paints  
• Soluble in aliphatic solvents |
| ![molecule](phenolic-resins) phenolic resins (e.g. bisphenol A) | • Resistant to water, alkali, grease and oil  
• Hard surface  
• Glossy finish |

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1Unfortunately, despite its very useful features, abietic acid results in resins which are brittle and have poor durability.
The monomers are substances that are able to be polymerised by free-radical polymerisation, i.e. they have a double bond. Some common monomers are:

- Vinyl acetate (CH₂=CH-O-C=O)
- Styrene (CH₂=CH-C₆H₅)
- Methyl methacrylate (CH₂=CH-C=O-O-CH₃)
- Butyl methacrylate (CH₃-CH₂-CH₂-CH₂-CH₂-C=O-O-CH₃)
- Acrylonitrile (H₂C=CH-CN)

Hence the resulting products are often termed 'acrylics'.

The polymerisation of the monomers is caused by the initiators. These are often persulphates, and are commonly 'activated' (decomposed into free radicals) by iron(II):

\[
S₂O₈^{2-} + Fe^{2+} \rightarrow SO₄^{2-} + SO₄^{−} + Fe^{3+}
\]

The free radical then starts the polymerisation reaction, shown here with styrene:

**initiation**

\[
\text{CH} = \text{CH}_2 \text{OSO}_3^- + \text{CH} = \text{CH}_2 \rightarrow \text{CH} = \text{CH}_2 - \text{CH} = \text{CH}_2 - \text{SO}_4
\]

**propagation**

\[
\text{SO}_4^{−} + \text{CH} = \text{CH}_2 \rightarrow \text{CH} = \text{CH}_2 \text{OSO}_3^-
\]

**termination (by recombination)**

\[
\text{CH} = \text{CH}_2 + \text{H}_{2} \text{C}^* \text{OSO}_3^- \rightarrow \text{CH} = \text{CH}_2 \text{H}_{2} \text{C}^* \text{OSO}_3^-
\]

A formulated blend of these monomers is polymerised in water under controlled temperature conditions as the reactions are exothermic. Initiators such as ammonium persulphate are added to start the free-radical polymerisation. Activators such as ferrous ammonium sulphate.
are also added to speed up the dissociation of the initiators and hence increase the concentration of radicals. Emulsifiers or surfactants are added to stabilise the emulsion. The final product consists of a suspension of polymer micelles whose diameter is between 0.1 and 1.0µm. Each micelle is coated by a layer of emulsifier, one end of which is attached to the particle while the other extends into the surrounding water, thereby holding the micelle in a stable suspension (see industrial resins article).

**Epoxy resins**

Epoxy resins are derived from the simple organic compound oxirane - ethylene oxide.

![Ethylene Oxide](image)

The commonest starting products for epoxy resins are epichlorhydrin and bisphenol A:

![Epichlorhydrin and Bisphenol A](image)

The simplest epoxy resin from these ingredients is the diglycidyl ether formed by reacting 2 moles of epichlorhydrin with 1 mol of bisphenol A:

![Diglycidyl Ether](image)

Epoxy resins may be low viscosity fluids or high molecular mass solid resins. Epoxy resins may be used to form films if they are polymerised by the addition of suitable 'curing' agents. The epoxy group will react with active hydrogen\(^2\)-containing nucleophiles such as H\(_2\)O, Grignard reagents and HX (where X = F, Br, Cl or I) to form a hydroxyl group. The commonest nucleophile which is used in the paint industry is the amino group contained in amines or amides:

![Epoxy Resin Polymerisation](image)

The secondary amine formed may react with another epoxy group:

\[ \text{R–NH}_2 + \text{H}_2\text{C–CH–R'} \rightarrow \text{R–NH–CH}_2\text{–R'} \]

**secondary amine**

\(^2\)A hydrogen with a \(\delta^+\) charge that will be attacked by the \(\delta^-\) charge of the oxygen in the epoxide group.
By use of amines or amides possessing a minimum of three active hydrogens a three dimensional polymeric structure may be built up.

Epoxies may be modified with many other resins such as phenol-formaldehydes, urea-formaldehydes, melamines, alkyds or even drying oils to produce resins having a very wide range of properties. Epoxies are usually only used in industrial and marine areas and restricted to use as primers and intermediate build coats due to their poor performance on exposure to UV. They are often used in conjunction with a polyurethane topcoat.

**Polyurethanes**

These have been developed from a reaction discovered by O. Bayer in Germany in the 1930s. Bayer A. G. is amongst the world leaders in the manufacture of resins used in polyurethane paints. Urethanes may be considered to be the reaction product of the addition of H—O over the N=C of an isocyanate group:

\[
\text{HO—R—OH } + \text{ O—C=N—R'—N=C=O } \rightarrow \text{ HO—R—O—C—NH—R'—N=C=O}
\]

Polyurethane paint systems have been developed which are characterised by tough, durable films which retain their gloss for long periods and which are very resistant to weathering. They are often very easy to clean. Polyurethanes are commonly used for painting aircraft.

There are very many other synthetic resins which are used in the manufacture of paints and these include phenol-formaldehydes, urea-formaldehydes, melamines, vinyls, acrylic resins and chlorinated rubber.

**Pigments**

Pigments serve three main functions: the optical function of providing colour, opacity and gloss; a protective function with regards to the surface underneath the paint and with regards to the binder which can be destroyed by UV; and a reinforcing function for the paint itself in that they help the binder to stick. Pigments are composed of tiny solid particles less than 1µm in diameter, a size that enables them to refract light (light has wavelengths between 0.4µm and 0.7µm).
For the pigment to be effective it has to be evenly dispersed throughout the solvent\(^3\) and in contact with the solvent. Surrounding pigment particles is a layer of moist air and, in some cases, other gases. To bring the pigment into contact with the solvent this layer has to be displaced, and this displacement is known as wetting. If a pigment is not properly wetted in a paint it may result in colour streakiness in the finished paints, thus solvents and pigments must be chosen that result in a well wetted pigment. Wetting and dispersing agents are used to improve the wetting properties of the resin/solvent system.

A variety of natural and synthetic pigments are used in paints, providing a complete spectrum of colours and a variety of finishes. Pigments are broadly classified as either organic (Table 3) or inorganic (Table 4). In organic pigments the colour is due to light energy absorbed by the delocalised B electrons of a conjugated system\(^4\). The electrons do not usually absorb all wavelengths of light, so some frequencies are allowed to pass through. It is this unabsorbed light that we see, so the colour of a given pigment is the opposite colour of the frequencies absorbed by the molecule. The greater the number of conjugated bonds in a system, the lower the energy of light absorbed, thus a molecule with little or no conjugation will absorb in the UV (and hence appear white), whereas one with more conjugation will absorb in the blue and appear yellow, or in the green and appear red etc. Functional groups that absorb visible light (and hence appear coloured) are called 'chromophores', and some of the more common ones are —N=N—, —C=C—, —C=O, —C=S, —C=NH, —N=O, —NO\(_2\).

Organic pigments are usually preferable as in general they are:

- brighter
- stronger (although this varies greatly between organic pigments)
- more transparent (this is not always an advantage)
- more stable

In addition they have greater tinting strength (i.e. less pigment is required to get an equally strong colour), better gloss development and some absorb UV light, preventing it from damaging the binder.

However, inorganic pigments are also widely used as they do not bleed, are heat and light stable and are much cheaper than organic pigments. In addition they are used for some specialist pigments (such as anti-corrosion pigments), and for black and white pigments, as it is not possible to get pure black or white organic pigments. One such white pigment, titanium dioxide, is widely agreed to be the single most important pigment in use today. It is the strongest known pigment in terms of both opacity and tinting power which, coupled with its pure white tint and its fine particle size, means that it can be used as an opacifier to prepare films with a high hiding power and reduced pigment content. This has resulted in paints with much improved elasticity and hence improved durability.

\(^3\)In this context the solvent includes water as well as organic solvents.

\(^4\)A conjugated system is one consisting of alternating single and double bonds in which the B electrons are delocalised, i.e. the electrons of the second electron pair of the double bond (the B electrons) are free to move between all the conjugated atoms.
<table>
<thead>
<tr>
<th>Group</th>
<th>Example</th>
<th>Colour†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo dyes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoazo</td>
<td><img src="image" alt="Monoazo structure" /> arylamide yellow (PY 73)</td>
<td>✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>Diazo</td>
<td><img src="image" alt="Diazo structure" /> diarylide yellows</td>
<td>✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>Azo condensation</td>
<td><img src="image" alt="Azo condensation structure" /></td>
<td>✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>Azo salt</td>
<td><img src="image" alt="Azo salt structure" /> Barium red 2B toner (PR 48.1)</td>
<td>✓ ✓ ✓ ✓</td>
</tr>
</tbody>
</table>

Table 3* - Some common classes of organic pigments**

X-Polymers-D-Paints and Pigments-13
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo metal complex</td>
<td><img src="image" alt="Structure" /></td>
<td>nickel azo yellow (PG 10)</td>
</tr>
<tr>
<td>Benzimidazolone</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Polycyclic pigments</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Phthalocyanide</td>
<td><img src="image" alt="Structure" /></td>
<td>copper phthalocyanine</td>
</tr>
<tr>
<td>Pigment</td>
<td>Structure</td>
<td>1</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>---</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>dibrom anthanthrone</td>
<td>✓</td>
</tr>
<tr>
<td>Quinacridone</td>
<td>quinacridone red (PV 19)</td>
<td>✓</td>
</tr>
<tr>
<td>Dioxazine</td>
<td>dioxazine violet (PV 23)</td>
<td></td>
</tr>
<tr>
<td>Perylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thioindigo</td>
<td>tetrachloro thiondigo (PR 88)</td>
<td></td>
</tr>
</tbody>
</table>

* Table based on Table 27.1 of "Surface Coatings" (see acknowledgements)
** Other common pigments include nitro, nitroso, quinoline and azine pigments
† 1 = yellow; 2 = orange; 3 = red; 4 = brown; 5 = violet; 6 = blue; 7 = green
<table>
<thead>
<tr>
<th>Inorganic Pigments</th>
<th>Production</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Colour(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon black</strong></td>
<td>decomposition of carbonaceous matter</td>
<td>high strength, good colour, light &amp; weather resistant</td>
<td>thickens paint</td>
<td>black</td>
</tr>
<tr>
<td><strong>Titanium dioxide</strong></td>
<td>synthesised</td>
<td>high strength, high opacity, cheap, good UV resistance</td>
<td>forms radicals that degrade the binder</td>
<td>white</td>
</tr>
<tr>
<td><strong>Iron oxides</strong></td>
<td>usually mined although can be synthesised</td>
<td>light and weather resistant, unreactive</td>
<td>cannot produce clean shades</td>
<td>yellow, red, brown, black</td>
</tr>
<tr>
<td><strong>Zinc chromates</strong></td>
<td>synthesised according to reaction (1)</td>
<td>corrosion formed by reaction (2) is inhibited according to reaction (3)</td>
<td>thickens paint</td>
<td>yellow</td>
</tr>
<tr>
<td><strong>Azurite Na₃Al₆Si₄O₂₄S₂</strong></td>
<td>kaolin, Na₂CO₃, sulphur and carbon heated together above 800°C</td>
<td>rich colours</td>
<td>fades on contact with acid</td>
<td>blue</td>
</tr>
<tr>
<td><strong>Chromium oxides</strong></td>
<td></td>
<td>light, weather, alkali and acid resistant; thermally stable</td>
<td>doesn’t give clear colours</td>
<td>green, blue</td>
</tr>
<tr>
<td><strong>Cadmium sulphides</strong></td>
<td>reacting cadmium salts with sodium sulphide</td>
<td>heat and light resistant, clear pigment, high opacity</td>
<td>expensive, poor weather resistance</td>
<td>greenish yellow to red to bordeaux</td>
</tr>
<tr>
<td><strong>Lithopone ZnS mixed with BaSO₄</strong></td>
<td>synthesised according to reaction (4)</td>
<td>pure tints when mixed with organics, unreactive, easily wetted</td>
<td>poor weather resistance</td>
<td>white</td>
</tr>
</tbody>
</table>

(1) $4\text{ZnO} + 2\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{CrO}_4 + 3\text{ZnCrO}_4 \text{Zn(OH)}_2$
(2) $4\text{Fe} + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \text{H}_2\text{O}$ (spongy mass)
(3) $2\text{Cr}^{6+} + 2\text{Fe} + 6\text{OH}^- \rightarrow 2\text{Cr}^{3+} + \text{Fe}_2\text{O}_3$ (hard, protective coating) + $3\text{H}_2\text{O}$
(4) $\text{ZnSO}_4 + \text{BaS} \rightarrow \text{BaSO}_4(s) + \text{ZnS(s)}$
As stated earlier, pigments provide other properties to paints than just colour and hiding power. Anti-corrosive pigments are a very important area of study. Steel is probably the metal most often requiring protection against corrosion and the development of pigments to inhibit the corrosion of steel has occupied chemists for many years. The anti-corrosive pigment which has been used for many years in red lead, Pb₃O₄. In combination with linseed oil, red lead has in the past been the standard anti-corrosive primer for iron and steel. Unfortunately, red lead is toxic and much research has been, and is still being, carried out worldwide to find anti-corrosive pigments which are as effective as red lead. Anti-corrosive pigments for iron and steel commonly in use include zinc phosphate, zinc chromate, zinc molybdate and barium metaborate, although alternatives to chromates are being sought as they are toxic and environmentally hazardous.

Paints are often formulated with other mineral compounds included, which do not provide any staining power or opacity. These are known as extenders and are a very important part of the paint formulator's 'tool kit'. Extenders may be used to improve the application characteristics, as "flattening agents" to provide flat or semi-gloss finishes, to prevent settlement of pigments or provide better keying (sticking) properties for subsequent coatings. Common extenders are listed in Table 5.

Table 5 - Common extender pigments

<table>
<thead>
<tr>
<th>Common name</th>
<th>Formula</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>whiting</td>
<td>CaCO₃</td>
<td>undercoats and flat paints</td>
</tr>
<tr>
<td>talc</td>
<td>hydrated magnesium silicate</td>
<td>assists TiO₂ dispersion, improves sanding</td>
</tr>
<tr>
<td>barytes</td>
<td>BaSO₄</td>
<td>traffic paints (wear resistant), pigment extender</td>
</tr>
<tr>
<td>kaolin</td>
<td>hydrated aluminium silicate</td>
<td>assists TiO₂ dispersion, decreases viscosity</td>
</tr>
<tr>
<td>silica</td>
<td>SiO₂</td>
<td>flattening agent, traffic paints (wear resistant)</td>
</tr>
<tr>
<td>mica</td>
<td>hydrous aluminium potassium silicate</td>
<td>chemically and solar resistant, improves water resistance</td>
</tr>
</tbody>
</table>

One special type of pigment has become of importance in recent years - the metallic pigment. Many modern cars have metallic finishes and this appearance is due to the inclusion of finely divided aluminium. Bronze may also be used as a decorative pigment. Zinc and lead powders may also be used as pigments, but in this case the metal powder has anti-corrosive properties. Galvanic-type coatings containing zinc powder are an important tool in the protection of steelwork, and are the subject of continuous research and development.

**Solvents**

Solvents are necessary to ensure an even mixing of the paint components and to make them easy to apply. The solvents used differ with the way in which the paint will be applied as the drying rate required differs depending on the manner of application, e.g. the solvents in spray
paints need to evaporate much more quickly than those in brush-applied paints. In general, a blend of solvents is used to produce a paint that will surface and through dry (i.e. dry throughout) at the correct rate without uneven shrinkage. White spirit and mineral turpentine are probably the most widely used solvent, however many other compounds find use in paint formulation and these include:

\[ \text{toluene} \]

\[ \text{methylethyl ketone} \]

\[ \text{methyl isobutyl ketone} \]

\[ \text{xylene} \]

(usually a mixture of all three)

\[ \text{butylacetate} \]

\[ \text{1-methoxy-2-propyl acetate} \]

**ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS**

There is a pronounced movement worldwide to the development of high quality water-thinnable paints to supersede the current widely used organic solvent thinned paint. In the field of household paints there are now emulsion paints that provide performance equal to that of orthodox materials, but in the industrial paint field water thinnable paints are as yet only a minor percentage of the paints in use. Organic solvents are derived from petroleum. Many countries are reliant on expensive imported raw materials from which to produce their solvents. Very few paint manufacturing countries lack water. In addition, organic solvent vapours are atmospheric pollutants which in some cases can produce smog.
ROLE OF THE LABORATORY

It is the job of the paint technologist to carry out research and development with suitable binders, pigments and thinners in order to finally produce a paint which meets certain requirements set down by a customer. That customer may be a car manufacturer, who will require a total paint system for both decorating and protecting the very thin sheet steel of an automotive body. In that case, the paint will be required to have a high gloss and be resistant to fuel, oil and detergent. Its primer system must be able to slow the corrosion process. All this will be required of a system which may be less than 125µm in total thickness.

At perhaps the other end of the scale, the customer may be an engineer who wishes to protect the outside of steel tanks which are to be buried in the ground. In that case, the system will again be required to slow the corrosion of the steel, but appearance will not matter and, since the owner of the tank will not want to dig it up at regular intervals, it is likely that the total thickness may exceed 500µm.

Written by Michael D. T. Clark (formerly Senior Research Officer, Metal Protection Section, The Paint Research Association, Teddington, U. K.) with extensive revision and editing by Heather Wansbrough following correspondence with Steve Lipsham (Levene Paint Manufacturing Ltd.) and with reference to:

- Waldie, John M. (Chairman, textbook editing committee); *Surface Coatings. Volume 1 - Raw Materials and Their Usage*; Oil and Colour Chemists' Association, Australia; 1974, 1983