

# SURFACE COATINGS

## Objectives of coatings surfaces

Surface coatings, any mixture of film-forming materials plus pigments, solvents, and other additives, which, when applied to a surface and cured or dried, yields a thin film that is functional and often decorative. Surface coatings include paints, drying oils and varnishes, synthetic clear coatings, and other products whose primary function is to protect the surface of an object from the environment. These products can also enhance the aesthetic appeal of an object by accentuating its surface features or even by concealing them from view. Paints and lacquers are coatings that mostly have dual uses of protecting the substrate and being decorative, although some artists paints are only for decoration, and the paint on large industrial pipes is presumably only for the function of preventing corrosion. Protective coatings are unique method of corrosion control. They are used to give long term protection under a broad range of corrosive conditions, extending from atmospheric exposures to frill immersion in strongly corrosive solution. Protective solution provides little or no structural strength, yet they provide other material so that the strength and the integrity of a structure can be maintained.

The function of protective coatings is to prevent highly corrosive industrial fumes, liquids, solids, or gases from contacting the reactive underlying substrate of the structure. This physical separation of two highly reactive materials, the atmosphere and the substrate, is extremely important.

Those coatings are, in general, a relatively thin film separating the two reactive materials indicates the vital importance of the coating and the concept of a corrosion free structure. The coating must be, according to this concept a completely continuous film in order to fulfill its function. Any imperfection becomes a focal point for corrosion and the breakdown of the structure.

## COATING PROPERTIES

Corrosion resistant coatings must be characterized by many essential properties. These may vary, depending upon the specific use of the coating, but there are several basic characteristics required by all coating materials.

- **Water Resistance:** Resistance to water is perhaps the most important coating characteristic since all coatings will come in contact with moisture. Water is the universal solvent. Both iron and steel oxidize under even normal basic water conditions. There is no one coating that can be effective under all water conditions. The different types of water encountered only multiply these mechanical problems. Swamp water, which may be pure enough to drink, is ordinarily acidic and will corrode both steel and concrete. Sulfide water, which is prevalent in many areas, reacts readily with metals. High

conductivity water or seawater leads to rapid formation of anode-cathode areas on steel, which results in severe pitting. Pure water from the snowfields will dissolve calcium out of the concrete at a rapid rate, leaving the aggregate exposed. Water with high oxygen content will also create anode cathode type corrosion areas. The problem is thus a very complex one since no single type of material will provide a universal answer. For a high-performance corrosion-resistant coating shall have excellent water-resistant means that it must not only withstand continuous immersion in water or seawater, but it must do so without blistering, cracking, softening, swelling or loss of adhesion. It must also withstand repeated cycles of wet and dry conditions, since such coatings are normally exposed to an atmosphere of condensing dew in the evening and night hours and sun drying during daylight.

- **Chemical Resistance:** Chemical resistance is the ability of the coating, and particularly the resins from which it is formulated, to resist breakdown by the action of chemicals to which it is exposed. Chemical resistance depends on the both the coating formulation and on the resins from which the coating is produced. Generally, a coating which is considered chemical-resistant and which would be used for corrosion resistance in a chemical atmosphere should be resistant to salts, acids, and alkalis of a rather wide pH range. It should also be resistant to organic materials such as diesel oil, gasoline, lube oil, and similar materials, since these are compounds found in almost all industrial operations. Alkali resistance is, of course, extremely important in a primer. Since one of the chemical reactions in the corrosion process is the development of strong alkali at the cathode, any primer which is not highly resistant to alkali will tend to fail in the cathode area, resulting in undercutting of the coating and spreading of corrosion underneath the coating.
- **Proper Adhesion:** A corrosion-resistant coating must also be highly adherent. Since the property of adhesion is essential in preventing the effects of water on the life of the coating and in preventing the problems caused by a temperature gradient across the coating, adhesion is probably the key requirement in a corrosion-resistant coating. Irrespective of most of its other properties, the coating with very strong adhesion to the surface will retain its integrity much longer than one with less adhesion but other strong characteristics.
- **Abrasion Resistance:** Coatings, which are applied to ships, helicopter decks, barges, offshore platforms, and other similar areas, are excellent examples of why many corrosion-resistant coatings also require abrasion resistance. In these areas, coatings are subject to the movement of heavy equipment, foot traffic, possible wheel traffic and damage by tools and equipment. In order to withstand this type of service and remain effective as a corrosion-resistant film, a coating must be tough, extremely adhesive, hard and resistant to shock. The most effective abrasion-resistant organic coatings are the polyurethane coatings. These have exceptional resistance to impact, scouring and abrasion. Inorganic zinc coatings, however, because of their good adhesion to the steel

surface and because of their silicate and zinc composition, have proven outstanding when applied on the decks of barges and ships.

- **Ability of Expand And Contract:** Each coating material has a different coefficient of expansion. Any coating, which is to withstand corrosive conditions, must also have the property of expanding and contracting. Epoxies or atkyds may after some considerable aging, become brittle and cease to expand and contract. This can lead to cracking and spalling from the surface because of the temperature cycling. A proper corrosion resistant coating must withstand temperature changes without loss of adhesion and without checking or cracking. Inorganic zinc coatings have proven to have exceptional resistance to such changes in temperature.
- **Weather Resistance:** A weather-resistant protective coating must withstand the sun's rays, rain, snow, dew, freezing, and thawing, expansion and contraction of the substrate, chemical fumes, dusts, as well as continuing wet and dry cycling-usually on the daily basis. Weather resistance combines into one property almost all of the properties required of a coating for more specific uses. To be weather-resistant, a coating must resist the above conditions without excessive checking, chalking, flaking, blistering, loss of adhesion or substantial colour or appearance change.
- **Resistance To Bacteria And Fungus:** There are two ways in which bacteria and fungus can affect a coating. First, where they settle on any dirt that has accumulated on the surface of a coating, they tend to live and thrive. They attack on the coating and form colonies. These fungus colonies are living on one or more of the coating ingredients and can eventually lead to premature coating breakdown. Underground conditions can also lead to coating breakdown due to bacteria attack.
- **Pleasing Appearance:** Although a coating is primarily used to prevent corrosion and protect the basic structure, it should also be pleasing to the eye and maintain its colour.
- **Easy Application:** Application is one of the most important coating characteristics, especially when dealing with structures with many comers, edges, recesses, and similar areas. If a coating is somewhat difficult to apply, these are the areas which suffer and which breakdown first in the corrosive atmosphere.
- **Resistance To Extreme Temperature:** While all coatings are subjected to temperature and come temperature cycling, these conditions are generally moderate. Temperature, however, can be key factor in coating used for stacks, pipes, the exterior of process vessels, and for other similar uses. Where coating is used for excessively cold temperatures the three general characteristics to be considered are adhesion, shrinkage, and brittleness.
- **Radiation Resistance:** Atomic energy and atomic power coatings have been used extensively for protection against the radioactive contamination of various substrates including steel, concrete, stainless steels etc. in order to be effectively used on such installation, coatings must be able to withstand varying amounts of radiation.

- **Friction Resistance:** Some coatings are subject to friction, particularly when they are used as faying surface where two sections of metal are riveted or bolted together to form a friction joint. Inorganic coatings have proven to be very satisfactory under such conditions, while most organic coatings are unsatisfactory.

## **TYPES OF COATINGS:**

No one expected to be a chemist; however, some basic knowledge of the different types of coating materials and their chemical and physical properties as explained earlier can be advantageous. Generic coating types take their name from the resin in their formulation. Thus a coating may be referred to as a vinyl or an epoxy, although it may be highly modified, or in some cases, it may be combination of two or more different resins, one of which will usually be predominant. For example, vinyl resins are often modified with alkyd or acrylic resins, or coal tar pitch may be used in conjunction with epoxy resins. Such modifications produce the thousands of combinations today. The most common generic types of coatings are.

1. Acrylics, 2. Alkyds, 3. Bituminous, 4. Chlorinated rubbers, 5. Epoxy amine, 6. Epoxy coal tar, 7. Epoxy ester, 8. Epoxy Phenolic, 9. Epoxy polyamide, 10. Inorganic and organic zincs, 11. Silicones, 12. Urethanes, 13. Vinyls.

The more significant features of the different generic types of coating materials are as follows:

1. **Acrylics:** Acrylics have excellent colour and gloss retention for outdoor applications and are often combined with other resins because of these properties. They are ideal for use in areas of mild chemical fumes but are not recommended for tank linings. They are somewhat inferior to vinyls or chlorinated rubbers in chemical resistance. They cure by solvent evaporation. They are often used as a topcoat over other chemical resistance coatings are applied, because of their color and gloss retention.
2. **Alkyds:** Alkyds are usually natural oils that have been chemically modified to improve the rate of cure, chemical resistance and hardness. They are general-purpose coatings designed for applications to a wide range of substrates. They are easily applied and can be used as primers or topcoats. They provide good colour retention and gloss but exhibit poor chemical resistance. Since they are subject to saponification, which is chemical interaction of fat with an alkali that forms a soap, they are not suitable for applications to alkaline surfaces. They cure by air oxidation.
3. **Bituminous:** Bituminous coatings are low-cost, heavy-bodied materials applied either hot or as a air back with solvent. They provide good moisture barriers, have good-to-fair resistance to chemical fumes and spillage and exhibit good acid resistance and poor solvent resistance. They form very heavy films but have no corrosion inhibiting qualities. When they are

damaged, undercutting can be serious problem. They are available in black only. Materials such as clay, slate, mica, asbestos and other powders are sometimes added to increase film thickness and toughness. They cure by solvent evaporation.

4. **Chlorinated Rubber:** Chlorinated Rubber coatings are similar to vinyls in that they form fairly rough, thin films that have good abrasion resistance. They have excellent weathering properties and provide excellent resistance to most mineral acids and alkalis, salt and fresh water, and fungus growth. They are frequently modified with alkyd resins to lower their cost and improve their application characteristics. Curing is by solvent evaporation.
5. **Epoxy Amine:** Epoxy amine coatings are catalysed or hardened by an amine curing agent. These materials form a hard, abrasion resistant coating with good-to-excellent alkali, acid, and solvent resistance. They must be applied to a thoroughly cleaned surface and are moisture-sensitive during application. They have a tendency to fade and chalk in direct sunlight and to embrittle on ageing.
6. **Epoxy Polyamide:** Epoxy Polyamide coatings are not as resistant to acids, alkalis, or solvents as the amines. Polyamides have greater flexibility and provide water and salt solution resistance. They have a tendency to fade and chalk indirect sunlight and do not embrittle as much as the amine epoxies do on ageing.
7. **Epoxy Coal Tar:** Amine or polyamide epoxy resins are often modified with coal tar pitch to produce relatively high film build-up for good chemical and moisture resistance. Resistance to hydrogen sulphide and acids in general is dramatically improved over a straight epoxy. They have a tendency to embrittle on ageing, and delamination between coats or beneath touch-up patches is common unless special pre-cautions are taken during applications. They are normally black in colour.
8. **Epoxy Phenolic:** Epoxy Phenolic coatings combine a portion of Phenolic resin with epoxy resin. They are usually employed as tank linings but have been used extensively in nuclear plants, as interior coatings for vessels. They have good resistance to the effects of radiation.
9. **Epoxy Ester:** Epoxy ester coatings are a combination of an epoxy resin and a drying oil. These coatings cure by a combination of solvent evaporation and oxidation. They do not require the use of catalyst or hardener. Chemical resistance is better than alkyds but still rather poor. However, they can be applied by relatively inexperienced painter on surface having only marginal surface preparation. They do not lift most old, sound paints. Their weather resistance is fairly good, but they will chalk and yellow after extended exposure to sun. They do not saponify over alkaline surfaces to the same degree as an alkyd.
10. **Inorganic And Organic Zincs:** Metallic Zinc is used as the pigmentation with the variety of vehicle for inorganic and organic zinc coatings. They may be one- two- or three-package materials, post cured, moisture cured, solvent based or water based. The end product in all cases is metallic zinc suspended in extremely hard, tough silicate matrix. Acid or alkali resistance is poor but solvent, moisture and salt resistance is excellent. Their weather resistances are extremely well and are often used as a single coat system for structural steel or

tanks. Abrasive blasting is required, and the dry film thickness of the applied film is critical.

- 11. Silicones:** Silicone coatings are semi-inorganic polymers which, when formulated into coatings, have outstanding heat resistance and excellent water repellency. Properties depend on the amount of silicone resin and the type of modifying agents used (i.e. alkyd, acrylics, etc). In high heat applications, such as stoves, they are used to temperatures as high as 1200° F.
- 12. Urethanes:** Sometimes called polyurethanes or isocyanates, these coatings are a fairly new development but may be obtained in a wide range of formulations. Normally, two-package, catalysed materials, the aliphatic urethanes are hard, tough and abrasion resistant, with excellent weathering properties and gloss retention. They exhibit excellent solvent resistance, only slightly inferior to that of an epoxy, and withstand mild acids and alkalis. Their adhesion properties are excellent; however, they are usually applied over an epoxy primer. Urethanes can be applied at lower than most other chemically cured coatings. During applications, urethanes are moisture sensitive, but after they have cured, they exhibit outstanding resistance to high humidity.
- 13. Vinyls:** Vinyls are thermosetting materials and cure solely by solvent evaporation. As such, they can be applied at much lower temperatures than any catalysed coating. Acid and alkali resistance is excellent, but solvent resistance is poor. Because they are soluble in their own solvents, repairs are easily made. Water and weather resistance is outstanding characteristics. A clean, preferably abrasive blasted surface is required for proper adhesion. They usually employ special primers.

### **The components of paint**

The composition of a paint is indicated in the following Table, which also indicates the function of the main components. Not all paints have every ingredient. For example gloss paints will not contain extenders which are coarse particle inorganic materials. These are used in matt paints such as the surfacers or primer surfacers used in the motor industry. Major differences occur between the polymers or resins that are used in paints formulated for different purposes. This is because of differences between the methods of application and cure, the nature of the substrate, and the conditions of use. Thus architectural ('decorative' or 'household') paints will be required to be applied *in situ* at ambient temperatures (which may be between 7 and 30 °C depending on climate and geographical location). They will 'dry' or 'cure' by one of two mechanisms: (i) atmospheric oxidation or (ii) the evaporation of diluent (water) accompanied by the coalescence of latex particles comprising the binder. Many industrial finishing processes will require the use of heat or other forms of radiation (UV, IR, electron beam) to induce chemical reactions, such as free radical or condensation polymerization, to convert liquid polymers to highly crosslinked solids. The most common of these processing methods uses 'thermosetting' polymers which will frequently be admixtures of two quite different chemical types of material, e.g. alkyd combined with amino resin. There is a similarity between both the oxidative drying and industrial thermosetting processes in so far that in both cases the polymers used are initially of low

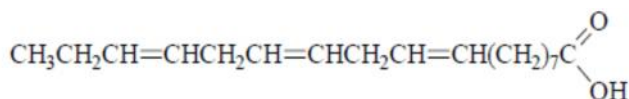
molecular weight and the curing process leads to crosslinking of these polymers to yield highly complex extremely high molecular weight products. In contrast, it is possible to produce coatings without the need for crosslinking, for use in both of these distinctive markets. In the case of decorative or architectural paints this is exemplified by the emulsion paint, in which the binder is in the form of high molecular weight polymer particles suspended in an aqueous medium. Lacquers used in the motor industry may be based upon high molecular weight polymer in solution. Both systems avoid the need for crosslinking to achieve satisfactory film properties, but recent technological developments suggest that improved film properties can be achieved by the introduction of crosslinking in some form, e.g. by the use of microgels.

#### The composition of Paints:

	Components	Typical function
Vehicle (continuous phase)	Polymer or resin (Binder)	Provides the basis of continuous film, sealing or otherwise protecting the surface to which the paint is applied. Varies in chemical composition according to the end use.
	Solvent or diluent	The means by which the paint may be applied. Avoided in a small number of compositions such as powder coatings and 100% polymerizable systems.
Pigment (discontinuous phase)	Additives	Minor components, wide in variety and effect, e.g. catalysts, driers, flow agents.
	Primary pigment (fine particle organic or inorganic)	Provides opacity, colour, and other optical or visual effects. Is thus most frequently used for aesthetic reasons. In primers the pigment may be included for anti-corrosive properties.
	Extender (coarse particle inorganic matter)	Used for a wide range of purposes including opacity/obliteration (as an adjunct to primary pigment); to facilitate sanding, e.g. in primer surfacers.

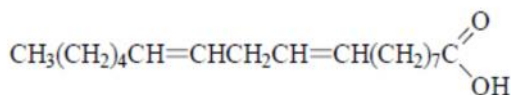
### Binders

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:



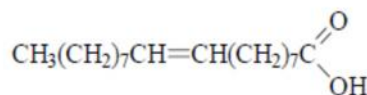
linolenic acid

(*cis, cis, cis* -9, 12, 15 - octadecatrienoic acid  $\text{C}_{18}\text{H}_{30}\text{O}_2$ )



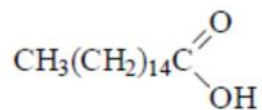
Linoleic acid

(*cis, cis* -9, 12 - octadienoic acid  $\text{C}_{18}\text{H}_{32}\text{O}_2$ )

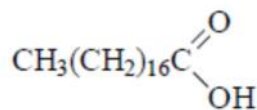


Oleic acid

(*cis* -9, - octadecenoic acid  $\text{C}_{18}\text{H}_{34}\text{O}_2$ )



Palmitic acid  
(hexadecanoic acid)  
 $\text{C}_{16}\text{H}_{32}\text{O}_2$

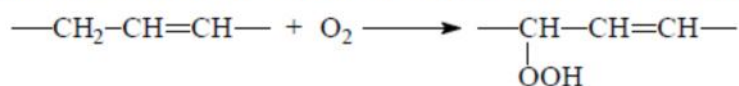


Stearic acid  
(octadecanoic acid)  
 $\text{C}_{18}\text{H}_{36}\text{O}_2$

Many common drying oils contain these compounds and others, including eleostearic and ricinoleic 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:

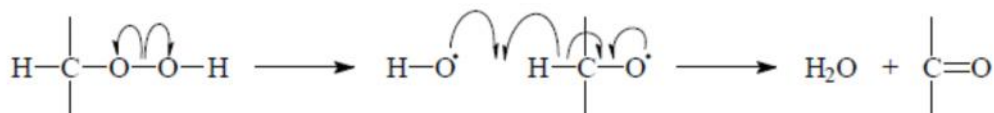
1. double bonds are oxidised by atmospheric oxygen to give hydroperoxy groups:



2. these peroxides then decompose to give radicals:



3. the radicals then initiate various polymerisation reactions:

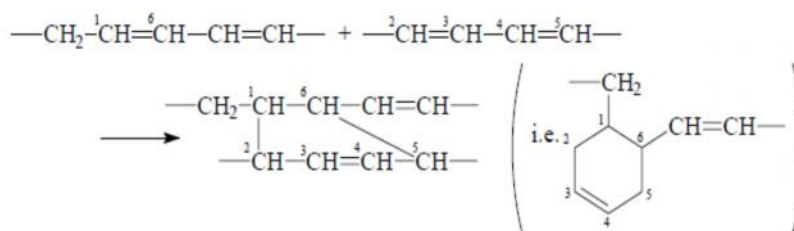


4. before recombining:

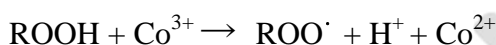




Other reactions also occur, including the Diels-Alder reaction:



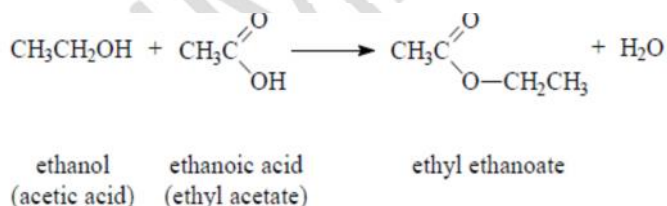
The drying process may be accelerated by the addition of small quantities of metals such as lead, cobalt or manganese compounds. These are 'driers'. Lead compounds are rarely used in modern paints due to their high toxicity. Driers catalyse peroxide decomposition as follows:



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.

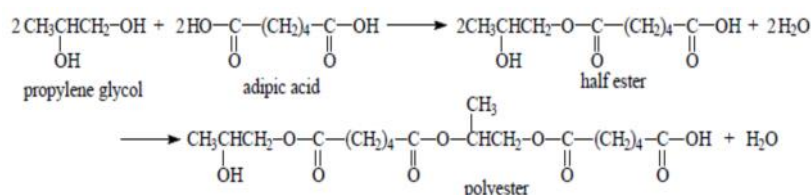
### Alkyd resins

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:

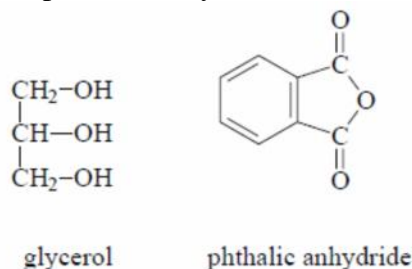


Esters formed in this type of reaction from monofunctional constituents are chemicals of fixed, known and easily determined molecular mass and structure. They are non-resinous (many natural and artificial flavours are esters).

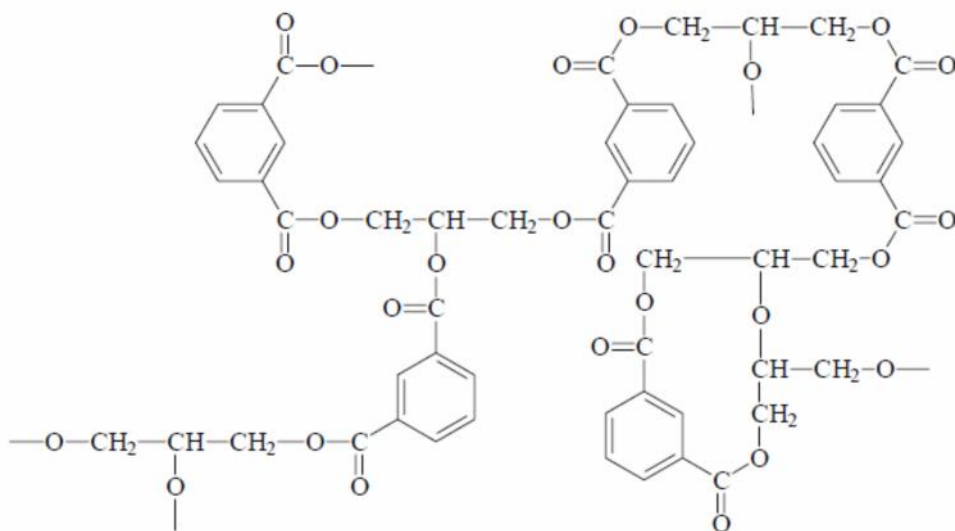
If polyfunctional ingredients are used, more complicated reactions occur:



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.



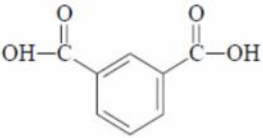
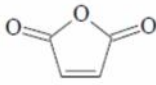
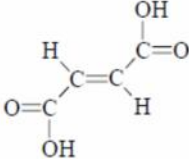
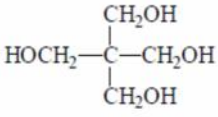
A portion of the complex glycerylphthalate resin would look as follows:



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.

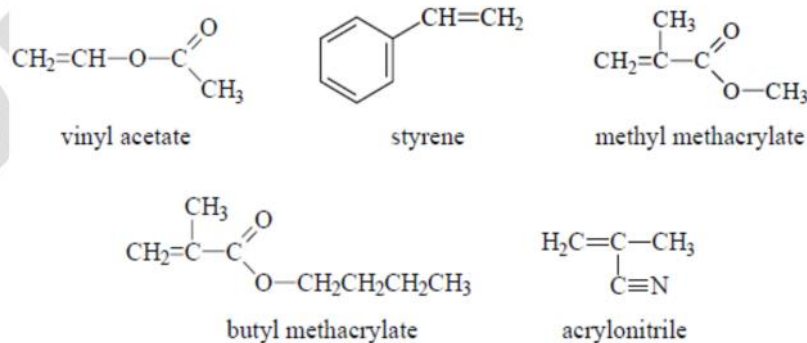
Table 1 - Alcohols and acids used in the manufacture of alkyd resins

Polyhydric alcohols	Dibasic acids
$\text{HOCH}_2\text{CH}_2\text{OH}$	
$\text{HO}-(\text{CH}_2)_n-\text{OH}$	
$\text{HO}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{OH}$	
	$\text{HO}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-(\text{CH}_2)_8-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$
	$\text{HO}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-(\text{CH}_2)_4-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$

### Emulsions

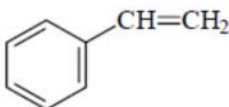
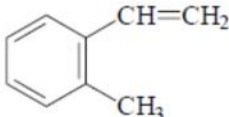
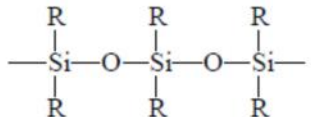
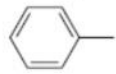
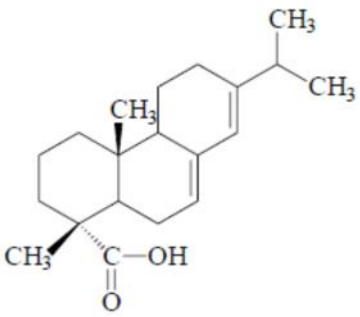
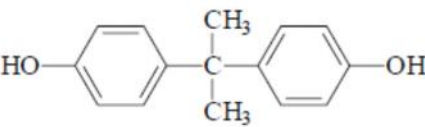
Alkyd paints consist of a pigment, solvent and binder which are all mutually soluble. An emulsion paint, on the other hand, consists of pigment and solid or semi-solid polymeric particles dispersed in a continuous aqueous medium in which they are insoluble. This emulsion is made from monomers, initiators (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.

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:



Hence the resulting products are often termed 'acrylics'.

**Table 2 - Additives used in alkyd resins**

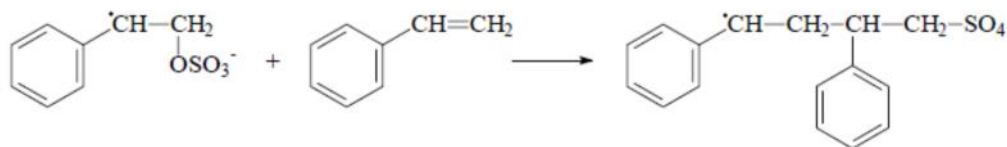
Additive	Function
	<ul style="list-style-type: none"> <li>• Reduce drying time</li> <li>• Improve durability of paint</li> </ul>
	<ul style="list-style-type: none"> <li>• Reduce drying time</li> <li>• Improve durability of paint</li> </ul>
 <p>where R is commonly methyl (CH<sub>3</sub>)</p> <p>or</p> 	<ul style="list-style-type: none"> <li>• Co-polymerise to make more durable glossy paints</li> <li>• Especially effective with dark paints</li> </ul>
 <p>abietic acid (rosin)<sup>1</sup></p>	<ul style="list-style-type: none"> <li>• Dries quickly</li> <li>• Produces glossy paints</li> <li>• Soluble in aliphatic solvents</li> </ul>
 <p>phenolic resins (e.g. bisphenol A)</p>	<ul style="list-style-type: none"> <li>• Resistant to water, alkali, grease and oil</li> <li>• Hard surface</li> <li>• Glossy finish</li> </ul>

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):

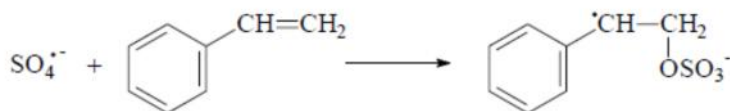


The free radical then starts the polymerisation reaction, shown here with styrene:

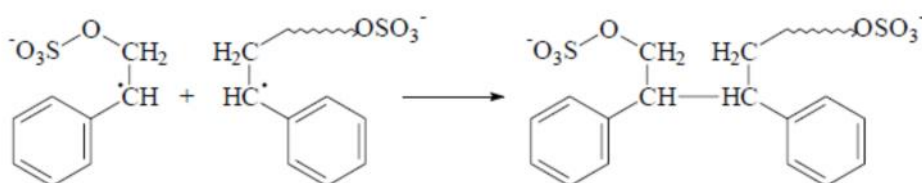
*initiation*



*propagation*



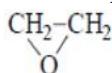
*termination (by recombination)*



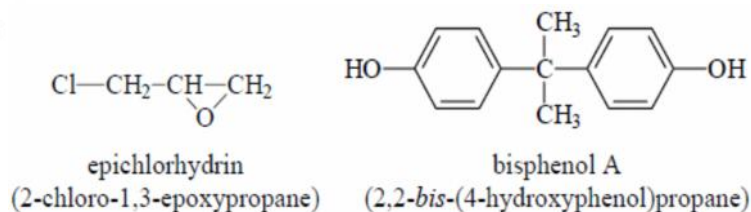
A formulated blend of these monomers is polymerised in water under controlled temperature conditions as the reactions are exothermic. Initiators such as ammonium persulphate are added to start the free-radical polymerisation. Activators such as ferrous ammonium sulphate are also added to speed up the 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 1.0  $\mu\text{m}$ . 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

### Epoxy resins

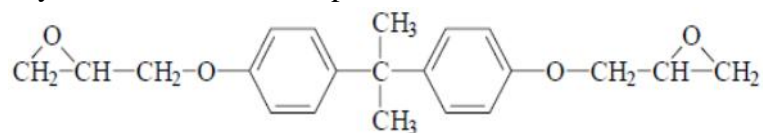
Epoxy resins are derived from the simple organic compound oxirane - ethylene oxide.



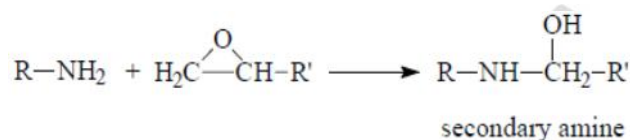
The commonest starting products for epoxy resins are epichlorhydrin and bisphenol A:



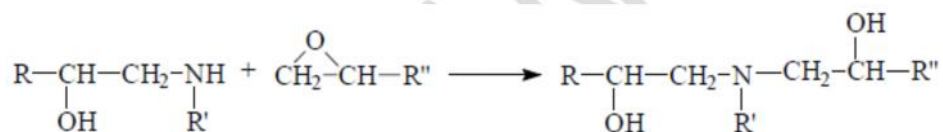
The simplest epoxy resin from these ingredients is the diglycidyl ether formed by reacting 2 moles of epichlorohydrin with 1 mol of bisphenol A:



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-containing nucleophiles such as  $\text{H}_2\text{O}$ , Grignard reagents and  $\text{HX}$  (where  $\text{X} = \text{F}, \text{Br}, \text{Cl}$  or  $\text{I}$ ) to form a hydroxyl group. The commonest nucleophile which is used in the paint industry is the amino group contained in amines or amides:



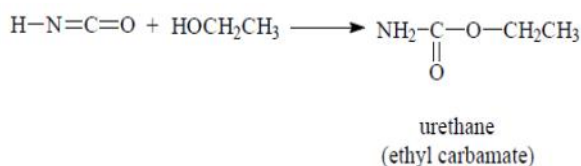
The secondary amine formed may react with another epoxy group:



By use of amines or amides possessing a minimum of three active hydrogens a three dimensional polymeric structure may be built up. Epoxy resins may be modified with many other resins such as phenol-formaldehydes, ureaformaldehydes, 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.

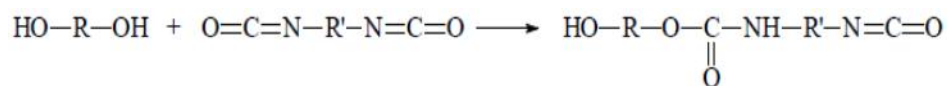
### ***Polyurethanes***

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  $\text{H}-\text{O}$  over the  $\text{N}=\text{C}$  of an isocyanate group:





Polyurethanes are derivatives of urethane which are produced from reaction of difunctional alcohols with difunctional isocyanates. They may be used in the manufacture of foamed plastics, elastomers and surface coatings and paints



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 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 electrons of a conjugated system<sup>4</sup>. 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<sub>2</sub>.

Organic pigments are usually preferable as in general they are:

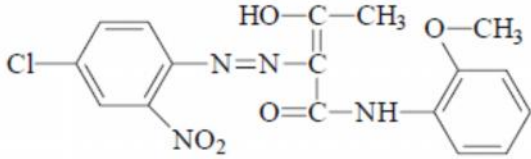
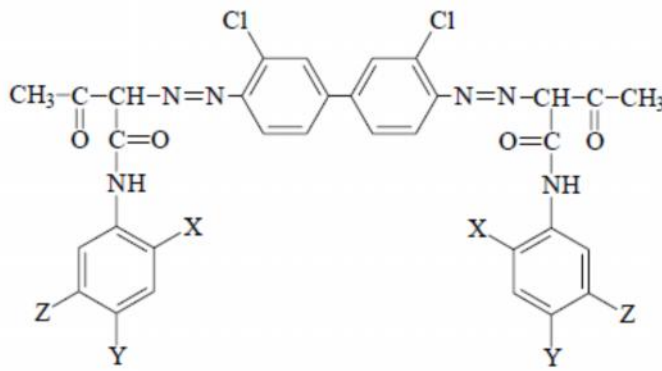
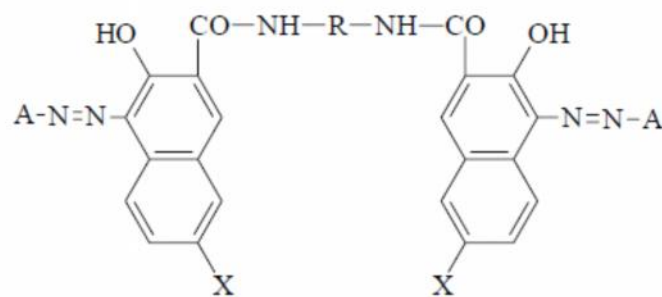
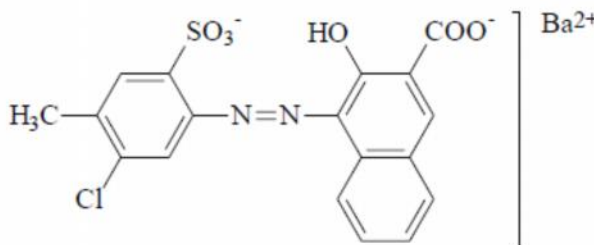
- brighter
- stronger (although this varies greatly between organic pigments)
- more transparent (this is not always an advantage)
- more stable

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.

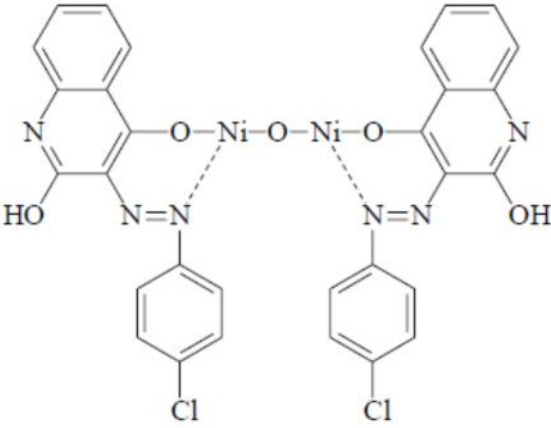
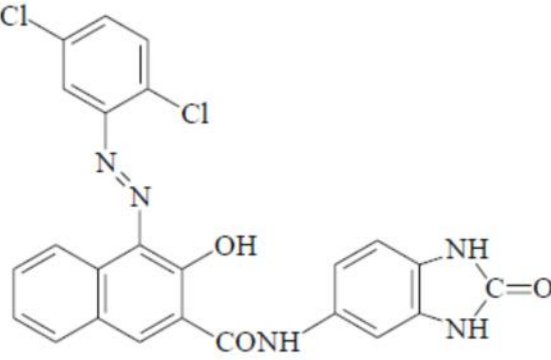
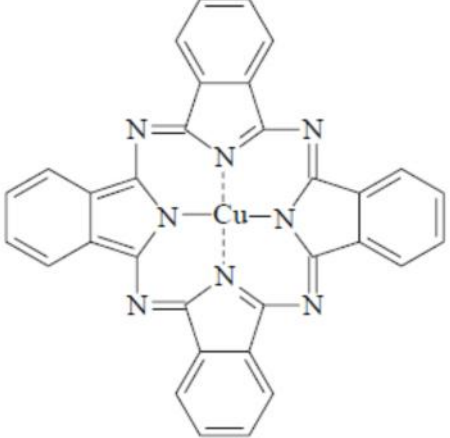
However, inorganic pigments are also widely used as they do not bleed, are heat and light stable and are much cheaper than organic pigments. In addition they are used for some specialist pigments (such as anti-corrosion pigments), and for black and white pigments, as it is not possible to get pure black 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.



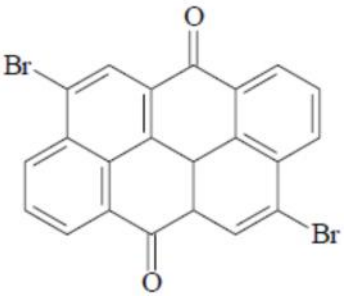
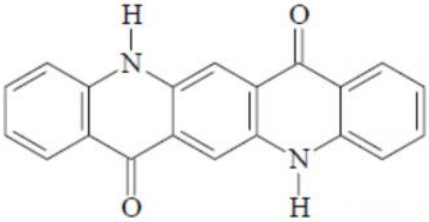
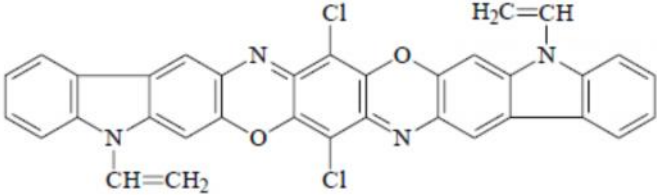
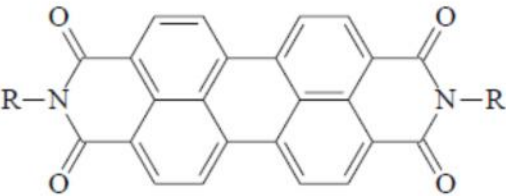
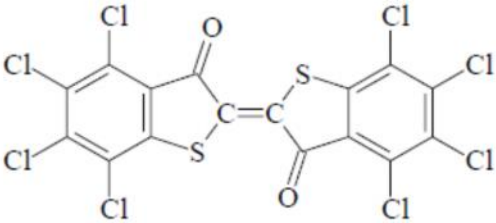
Table 3: Spme common class of Organic pigments

Group	Example	Colour†						
		1	2	3	4	5	6	7
Azo dyes								
Monoazo	<div></div> <p>arylamide yellow (PY 73)</p>	✓	✓	✓	✓	✓		
Diazo	<div></div> <p>diarylide yellows</p>	✓	✓	✓	✓		✓	
Azo condensation	<div></div>	✓	✓	✓	✓			
Azo salt	<div></div> <p>Barium red 2B toner (PR 48.1)</p>	✓	✓	✓	✓			

1 = yellow; 2 = orange; 3 = red; 4 = brown; 5 = violet; 6 = blue; 7 = green

Azo metal complex	 <p style="text-align: center;">nickel azo yellow (PG 10)</p>	<div>✓</div> <div>✓</div> <div></div> <div></div> <div></div> <div></div> <div></div> <div>✓</div>
Benzimi-dazolone		<div>✓</div> <div>✓</div> <div>✓</div> <div>✓</div> <div></div> <div></div> <div></div> <div></div>
Polycyclic pigments		
Phthalo-cyanide	 <p style="text-align: center;">copper phthalocyanine</p>	<div></div> <div></div> <div></div> <div></div> <div></div> <div></div> <div></div> <div>✓</div>

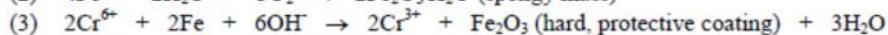
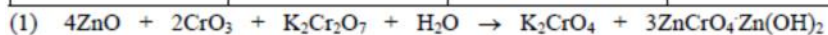
1 = yellow; 2 = orange; 3 = red; 4 = brown; 5 = violet; 6 = blue; 7 = green

Anthra-quinone	 <p>dibrom anthanthrone</p>	✓	✓	✓	✓	✓	✓	✓	✓
Quin-acridone	 <p>quinacridone red (PV 19)</p>	✓			✓		✓		
Dioxazine	 <p>dioxazine violet (PV 23)</p>						✓		
Perylene				✓	✓				
Thioindigo	 <p>tetrachloro thiondigo (PR 88)</p>						✓		

1 = yellow; 2 = orange; 3 = red; 4 = brown; 5 = violet; 6 = blue; 7 = green

**Table 4: Some common inorganic pigments:**

	Production	Advantages	Disadvantages	Colour(s)
<b>Carbon black</b>	decomposition of carbonaceous matter	high strength, good colour, light & weather resistant	thickens paint	black
<b>Titanium dioxide</b>	synthesised	high strength, high opacity, cheap, good UV resistance	forms radicals that degrade the binder	white
<b>Iron oxides</b>	usually mined although can be synthesised	light and weather resistant, unreactive	cannot produce clean shades	yellow, red, brown, black
<b>Zinc chromates</b>	synthesised according to reaction (1)	corrosion formed by reaction (2) is inhibited according to reaction (3)	thickens paint	yellow
<b>Azurite</b> $\text{Na}_7\text{Al}_6\text{Si}_4\text{O}_{24}\text{S}_2$	kaolin, $\text{Na}_2\text{CO}_3$ , sulphur and carbon heated together above $800^\circ\text{C}$	rich colours	fades on contact with acid	blue
<b>Chromium oxides</b>		light, weather, alkali and acid resistant; thermally stable	doesn't give clear colours	green, blue
<b>Cadmium sulphides</b>	reacting cadmium salts with sodium sulphide	heat and light resistant, clear pigment, high opacity	expensive, poor weather resistance	greenish yellow to red to bordeaux
<b>Lithopone</b> <b>ZnS mixed with <math>\text{BaSO}_4</math></b>	synthesised according to reaction (4)	pure tints when mixed with organics, unreactive, easily wetted	poor weather resistance	white



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 is red lead,  $\text{Pb}_3\text{O}_4$ . 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**.

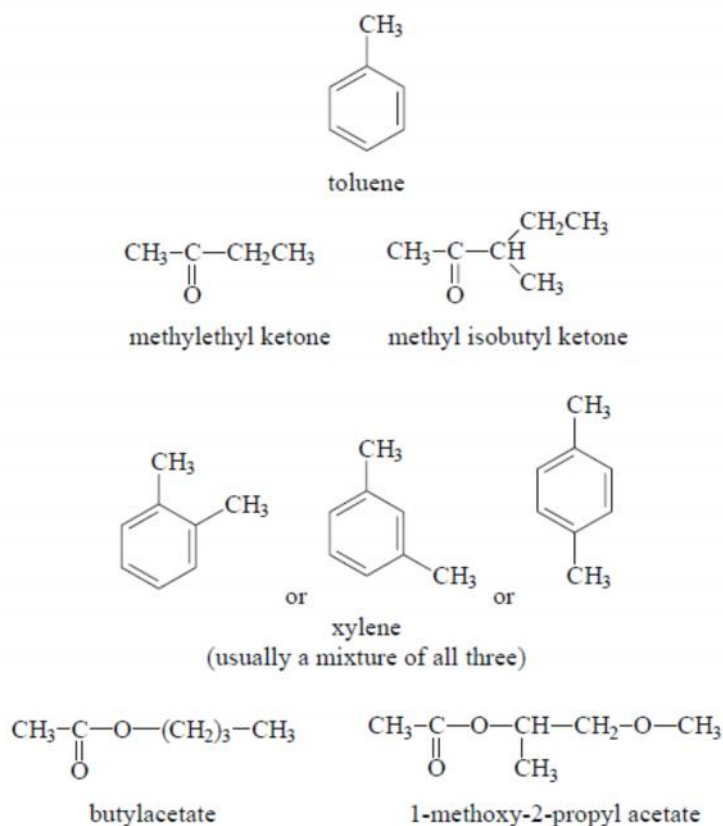
**Table 5: Common extender pigments**

Common name	Formula	Uses
whiting	$\text{CaCO}_3$	undercoats and flat paints
talc	hydrated magnesium silicate	assists $\text{TiO}_2$ dispersion, improves sanding
barytes	$\text{BaSO}_4$	traffic paints (wear resistant), pigment extender
kaolin	hydrated aluminium silicate	assists $\text{TiO}_2$ dispersion, decreases viscosity
silica	$\text{SiO}_2$	flattening agent, traffic paints (wear resistant)
mica	hydrous aluminium potassium silicate	chemically and solar resistant, improves water resistance

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:

**Paint additives:**

The simplest paint composition comprising a pigment dispersed in a binder, carried in a solvent (or non-solvent liquid phase) is rarely satisfactory in practice. Defects are readily observed in a number of characteristics of the liquid paint and in the dry film. These defects arise through a number of limitations both in chemical and physical terms, and they must be eliminated or at least mitigated in some way before the paint can be considered a satisfactory article of commerce.

Some of the main defects worth mentioning are settlement of pigment and skinning in the can; aeration and bubble retention on application; cissing, sagging, and shrivelling of the paint film; pigment flotation; and flooding. These defects represent only a small number of defects that can

be observed in various paints. It is perhaps worth-while to describe cissing, shrivelling, sagging, flotation, and flooding here.

- ‘cissing’ is the appearance of small, saucer-like depressions in the surface of the film;
- ‘shrivelling’ is the development of a wrinkled surface in films that dry by oxidation;
- ‘sagging’ is the development of an uneven coating as the result of excessive flow of a paint on a vertical surface;
- ‘floating’ is the term used for the colour differences that can occur in a paint film because of the spontaneous separation of component pigments after application;
- ‘flooding’ (also known as ‘brush disturbance’) is the permanent colour change of a paint subject to shear after application.

To overcome these defects their cause requires to be understood and a remedy found. In some cases the defect may be overcome by minor reformulation. Shrivelling, for example, is commonly due to an imbalance between the surface oxidative crosslinking of a film and the rate of crosslinking within the film. This can usually be overcome by changing the drier combination, which consists of an active transition metal drier such as cobalt which promotes oxidation and a ‘through’ drier such as lead or zirconium which influences crosslinking, but does not *per se* catalyse the oxidation process. In other cases simple reformulation will not provide a remedy, and specific additives have been developed to help in these cases. Thus anti-settling agents, anti-skinning agents, flow agents, etc. are available from specialist manufacturers for most defects and for most paint systems.

The problems of ‘floating’ and ‘flooding’ are associated with colloidal stability of the pigment dispersion and may arise from a number of different causes. The differential separation of pigment illustrated by floating occurs as a result of the differences in particle size of the component pigment and may be overcome by coflocculation of the pigments in the system. Another method of curing the condition may be to introduce a small proportion of a very fine particle extender such as alumina, of opposite surface charge to the fine particle pigment, to coflocculate with the latter.

The flooding (or brush disturbance) problem is indicative of flocculation occurring as a film dries. Under shear, as the brush disturbs the paint, the pigment is redispersed and the paint becomes paler in shade. This is because an increase in the back-scattering of incident light occurs, owing to the white pigment becoming deflocculated.

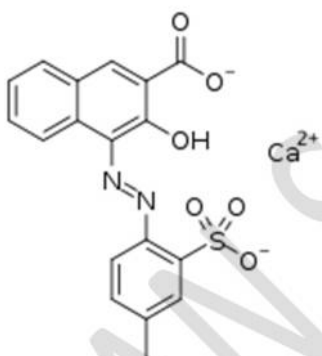
Cissing and sagging are illustrative of other aspects of physical properties associated with surface chemistry and rheology. In the former case, the effect is caused by a localized change in the surface tension of the film. In extreme cases this can give rise to incomplete wetting of the substrate, often distinguished by the term ‘crawling’. Sagging, on the other hand, is a bulk property of the film that may be influenced by the colloidal stability of the composition. Ideal, colloidally stable dispersions tend to exhibit Newtonian behavior, i.e. their viscosity is independent of shear rate. This means that on a vertical surface a Newtonian liquid that is of a suitable viscosity to be spread by a brush, i.e. with a viscosity of about  $0.5 \text{ Nsm}^{-2}$ , will flow excessively unless the viscosity rises rapidly as a result of solvent loss. Alternatively, the paint



formulator may aim to induce non-Newtonian behaviour such that the low shear viscosity of the product is very high. Thus, sagging may be avoided by either or a combination of these effects.

### **Lake pigment:**

A lake pigment is a pigment made by precipitating a dye with an inert binder, or "mordant", usually a metallic salt. Unlike vermilion, ultramarine, and other pigments made from ground minerals, lake pigments are organic. Manufacturers and suppliers to artists and industry frequently omit the lake designation in the name. Many lake pigments are fugitive because the dyes involved are not lightfast. Red lakes were particularly important in Renaissance and Baroque paintings; they were often used as translucent glazes to portray the colors of rich fabrics and draperies.



**A typical lake pigment is Lithol Rubine BK.**

### **Some important points:**

- A LAKE PIGMENT is an insoluble material that colours by dispersion.
- Lakes are basically a pigment which has been manufactured from a dye by precipitating a soluble dye with a metallic salt. The resulting pigment is called a lake pigment.
- Lakes are produced from the FD&C Dyes and are oil dispersible (but generally not oil soluble) and as such they can be mixed with oils, fats and sugars. They can also be dispersed in other carriers such as propylene glycol, glycerin and sucrose (water and sugar).
- Lakes are created in specific concentrations of the Dye which is used. As an example, Red 40 Aluminum Lake is available in Low Dye (generally 15-17% pure dye) and High Dye (36-42% pure dye).
- Lakes are generally preferred in several applications, including: To color an oil based product, such as balm base, chocolate or compound coatings.

### **Colour Stability:**

- Lakes are generally colour stable, meaning they resist bleeding.
- Dyes have a tendency to “bleed”, or migrate from one part of the product to another. A red and white soap may therefore become all pink in the future if dyes were used.



- Likewise with colour swirled lip balms or candy canes or any product where there are specific colour borders or stripes. In many cases Dyes can be used in confectionery production, Lakes will be substituted if bleeding is a problem.

### **Benefits of Lake Food Colors:**

- Lake food colors are highly adaptable and versatile: They can be dispersed in suspension of propylene glycol or sucrose.
- Lake colors are stable: Much more stable than water-soluble dye colors.
- Lake colors can be utilised to color many varieties of products and are commonly used in cosmetics and pharmaceuticals.
- Lakes are available in different concentrations of colors.
- Lake colors are oil soluble and can be mixed in vegetable oils, fats, other cosmetic oils etc.

### **Toner:**

Toner is a powder mixture used in laser printers and photocopiers to form the printed text and images on the paper, in general through a toner cartridge.

- Mostly granulated plastic, early mixtures only added carbon powder and iron oxide, however mixtures have since been developed containing polypropylene, fumed silica, and various minerals for tribo-electrification.
- Toner using plant-derived plastic also exists as an alternative to petroleum plastic. Toner particles are melted by the heat of the fuser, and are thus bonded to the paper.
- Toner is made up mostly of finely ground polyester, which is a type of plastic. Like your slacks sticking to your legs, polyester powder can hold a static charge that grabs onto anything with an opposite charge.

### **Emulsifier or Emulsifying agent**

An emulsifier or emulsifying agent is a compound or substance that acts as a stabilizer for emulsions, preventing liquids that ordinarily don't mix from separating. The word comes from the Latin word meaning "to milk," in reference to milk as an emulsion of water and fat. Another word for an emulsifier is an *emulgent*.

The term emulsifier may also refer to an apparatus that shakes or stirs ingredients to form an emulsion.

### *How an Emulsifier Works*

An emulsifier keeps immiscible compounds from separating by increasing the kinetic stability of the mixture. There are one class of emulsifiers, which lower surface tension between liquids or between a solid and liquid. Surfactants keep droplets from getting large enough for components to be able to separate based on density.

The method of emulsification matters in addition to the nature of the emulsifier. Proper integration of components extends the emulsion's ability to resist changes. For example, if you are making an emulsion for cooking, the mixture will maintain its properties longer if you use a blender than if you stir the ingredients by hand.

### *Emulsifier Examples*

Egg yolks are used as an emulsifier in mayonnaise to keep the oil from separating out. The emulsifying agent in egg yolks is lecithin.

Mustard contains multiple chemicals in the mucilage around the seed that act together as emulsifiers.

Other examples of emulsifiers include sodium phosphates, sodium stearoyl lactylate, soy lecithin, Pickering stabilization, and DATEM (diacetyl tartaric acid ester of monoglyceride).

Homogenized milk, vinaigrettes, and metalworking cutting fluids are examples of common emulsions.

### **Enamel paint:**

**Enamel paint** is paint that air-dries to a hard, usually glossy, finish, used for coating surfaces that are outdoors or otherwise subject to hard wear or variations in temperature.

Alkyds were the first 'enamels' (as opposed to physically drying 'lacquers') to be used for automotive refinish, bringing with them the great advantages of higher solids on application and hence higher build and 'gloss from the gun', eliminating the necessity for labour-intensive polishing. Alkyds are, however, slower to become 'dust-free' than lacquers, whether nitrocellulose or TPA, and hence must be applied in a dust-free environment. Their introduction was accordingly accompanied by the development of suitable spray booths for the car repair industry.

### **Acrylic enamel**

Acrylic enamels are alkyd/TPA copolymers which represent a hybrid product type, developed to improve the build and gloss of conventional TPA without losing the very rapid dust-free performance of the lacquer. The properties of these products fall accordingly between the two types. Like conventional alkyds they may be used as two-pack materials with a polyisocyanate second component. This confers benefits of through-drying speed, durability, and hardness, but loses all the benefits of the 'lacquer' drying, thus requiring dust-free application conditions.

## **Wax Polishing:**

Polishing is the process of creating a smooth and shiny surface by rubbing it or using a chemical action, leaving a surface with a significant specular reflection. In some materials (such as metals, glasses, black or transparent stones) polishing to minimal values.

When an unpolished surface is magnified thousands of times, it usually looks like mountains and valleys. by repeated abrasion, those “mountains” are worn until they are flat or just small “hills”. The process of polishing with abrasives starts with coarse ones and graduates to fine ones.

A wax is designed to enhance and protect a previously polished surface. Car wax is a non-abrasive coating usually containing Carnauba and other waxes. It is applied after washing your car and dries to a thin, milky-white layer when applied properly and is then wiped or buffed off with a microfiber towel. The wax serves as a clear, shiny protective layer between the elements and the clear-coat that has been applied over the paint on your car. It fills in very tiny (microscopic) dimples in the clear-coat and will help them shine to near-showroom brightness. The protection is necessary to keep airborne pollutants, road film, acid rain, and other contaminants from sticking to the surface, causing potentially long term damage.

*Main feature of wax polishing:*

- Use Paste wax as a buffer to shield the finish it covers, as well as to enhance its beauty.
- Carnauba wax, made from the leaves of a palm tree native to Brazil, is the most common ingredient in the most paste waxes.
- It is too hard to use on its own, but in combination with other ingredients, it protects well and polishes to a high gloss.