

Module 2: Introduction to Paint Technology

Basic Concepts of Paints

All objects are most vulnerable at their surfaces. It is the surface of any article that makes continual contact with the air, which may be moist, corroding or oxidizing. The surfaces of objects left in the open bear the brunt of the sun, rain, fog, dew, ice and snow. Under these conditions iron rusts, wood rots (or shrinks and cracks) and road surfaces crack and disintegrate. These, and more sheltered objects, suffer the wear of daily use, scratches, dents and abrasions - at their surfaces. To prevent or to minimize damage, various coatings are applied to these surfaces to protect them.

Coatings can also be used to decorate the articles, to add colour and lustre and to smooth out any roughness or irregularities caused by the manufacturing process. **Thus the function of any surface coating/paint is: 1) to protect 2) to decorate 3) to obliterate**

Paint can be defined as a fluid material which can spread over a surface in the form of a thin layer, forms a solid, adherent and cohesive film, after drying. Paints can be classified as decorative/architectural paints and industrial paints. As the names suggest, decorative paints are mainly used for household and construction purposes while industrial paints are used for the coatings of industrial products. On the basis of thinners, paints in turn classified into two types namely solvent based paints and water based paints.

Paint is a loosely used word covering a whole variety of materials, with names sometimes more descriptive of their composition or function: enamels, lacquers, varnishes, undercoats, surfacers, primers, sealers, fillers, stoppers and many others. It is essential to grasp at once that these and other less obviously related products, such as plasters, concrete, tars and adhesives, are all formulated on the same basic principles and contain some or all of three main ingredients.

First a pigment may be included. Pigments have both decorative and protective properties. The simplest form of paint is whitewash and, when dry, whitewash is nothing more than a pigment - whiting (calcium carbonate) - spread over a surface. It decorates and to some extent it protects, but it rubs off. So most paints contain the second ingredient, the film-former or binder, which will be a resin or polymer, to bind together the pigment particles and hold them on the surface. If the pigment is left out, the film-former covers and protects the surface, decorating it by giving it gloss or 'sheen'. It is difficult to attach coatings that are not fluid to any but the simplest of surfaces: those that are flat or gently curving. The fluidity of paint permits penetration into the most intricate crevices. It is achieved by dissolving the film-former in a solvent, or by colloidal suspension of both pigment and film-former in a diluent. Thus the third basic ingredient of paint is a liquid. Often the film-former-liquid mixture is called the vehicle for the pigment.

If the pigment is omitted, the material is usually called a **varnish**. The term clearcoat is used for unpigmented coatings applied over metallic paints. The pigmented varnish - the paint - is sometimes called an **enamel, lacquer, finish or topcoat**, meaning that it is the last coat to be applied and the one seen when the coated object is examined. **Lacquers** are normally thermoplastic solution paints or varnishes, but the term is sometimes (confusingly) used to describe all clear wood finishes. **Enamels** are normally thermosetting paints, hard, with a superficial resemblance to vitreous enamels.

General Ingredients & their functions

The fluid paints consist of the following ingredients:

- **Pigments and extenders**
- **Binders**
- **Solvents**
- **Additives**

Most of the coatings are described as solvent solutions or dispersion of some sort of binding medium. Usually called as resin in which is dispersed the solid inorganic, organic discrete phase known as the pigment. Depend upon the proportions of these resources can be obtained films with any desired physical and variety of application characteristics.

Pigments: Color pigments: These provide the paint's color. Inorganic pigments like titanium dioxide offer opacity and brightness, while organic pigments contribute to a wide range of colors.

Extenders: Increase the volume of the paint without significantly affecting its properties. Provide bulk and improve properties like hardness and durability. E.g. Calcium carbonate, talc, Clay, silica

Binder (Resin): The main component that binds the paint together. It forms a film after drying, providing adhesion and durability. Example: Vegetable Oils, Rosin, Nitrocellulose, Alkyd Resin, Polyurethane, Epoxy resin etc.

Solvents: These are used to dissolve or disperse the binder and pigments. They evaporate during drying, leaving the solid paint film. Example: Mineral spirits, turpentine, water:

Additives:

Thickeners: Control the viscosity of the paint.

Stabilizers: Prevent settling and separation of pigments.

Antifreeze agents: Prevent freezing during storage.

Defoamers: Minimize foam formation during manufacturing and application.

Drying agents: Accelerate the drying time of the paint.

Wetting agents: Improve the wetting of pigments by the binder, ensuring even distribution.

Biocides and Preservatives: Prevent the growth of bacteria, fungi, and mold in the paint.

Flow Sheet of Forms of Various Constituents of Paint

1. Pigment (Solid)

1. **Pigment (Solid)**
- 1. True Pigment
 - 1. Damp.
 - 2. Extender or transparent pigment
 - or hiding pigment
 - or prime pigment
 - They give hiding power
 - e.g. Titanium Dioxide
 - Cinnabar & Anatase
 - Zinc Oxide
 - Lead Chromate etc.
 - 2. Latent pigment
 - " colour etc.
- They are costly
(Pigment is not soluble in vehicle but dyer one soluble)

2. Vehicle (Liquid) or medium

2. **Vehicle (Liquid) or medium**
- 1. Non Volatile or Binder, former and film former
 - 1. Oil (Linseed, Coco etc)
 - gives flexibility
 - exterior durability
 - 2. Resin
 - gives hardness, toughness, adhesion etc.
 - 3. Plasticizer
 - gives flexibility
 - 4. Driers
 - act as catalyst
 - & reduce drying time of paint film.
 - 5. Calcium Carbonate of chalk, China clay, Barley, Bassot, Oyster shell, Chalk, They are very cheap, rather cheap.
 - 2. Volatile or solvent
 - 1. Reduces viscosity and brings paint in soluble form.
 - 2. Diluent or thinner (Toluene, M.T.O, Benzene, Xylene, Methyl Ethyl Ketone, Acetone, etc.)
 - 3. Latent solvent (Terpenes, e.g. Benzene, M.T.O, Toluene) cheaper

Understanding the functions of each component helps in formulating paints with specific properties such as adhesion, durability, color stability, and ease of application. The exact composition can vary depending on the type of paint (latex, oil-based, etc.) and its intended use (interior, exterior, industrial, etc.).

Introduction to drying oils

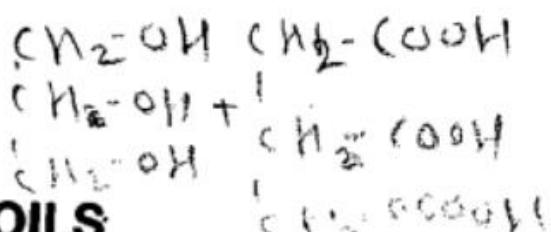
The oils used in the paint industry are derived mainly from vegetable and, to a much lesser extent, from animal sources. They are esters of glycerol and fatty acids, non-volatile, and unstable at high temperatures.

These oils vary in properties according to the nature of the fatty acids combined with the glycerol, i.e. they may be saturated or unsaturated. In the latter case, the oil possesses the valuable property of setting slowly to a solid and adherent film when spread on a surface and exposed to the air. This film formation is an irreversible process and the film is insoluble in white spirit. This process is known as 'drying' and the oils can be classified into the following groups based on their drying properties:

Drying oils, e.g. linseed-

Semi-drying oils, e.g. soya bean, tobacco seed

Non-drying, e.g. castor.

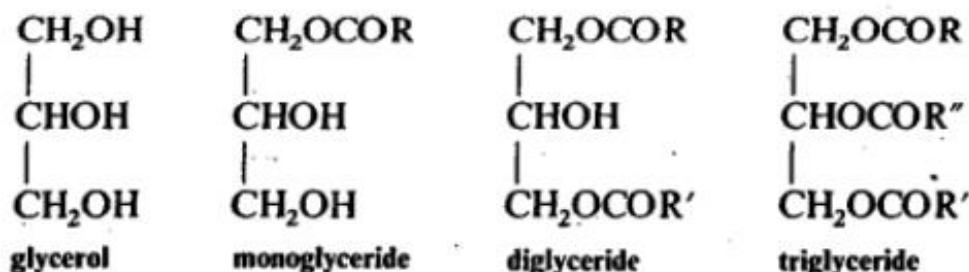


CONSTITUTION OF DRYING OILS

The esters produced by combination of glycerol with fatty acids are known as glycerides. A number of fatty acids are involved, so that the number of possible glycerides is large. Most oils consist of glycerides of several acids in varying proportions.

Glycerol (the pure material is known as glycerine) is a trihydric alcohol derived from propane. It is a colourless, viscous liquid, very hygroscopic and possesses the following constants: boiling point, 290°C (554°F); specific gravity (15°C) 1.265; refractive index 1.473.

As a trihydric alcohol, glycerol is capable of combining with one, two or three acid radicals to form mono-, di- and triglycerides. The constitution of these can be represented as follows, where R is a fatty acid chain:



Vegetable and animal oils consist mainly of the triglycerides with only small proportions of the mono- and diglycerides.

Fatty acids are a large group of compounds consisting of long hydrocarbon chains of about 16 carbon atoms and upwards, attached to a carboxyl (-COOH) group. They are usually straight chain compounds and are of two types (i) *saturated*, in which the four valencies of each of the carbon atoms are fully satisfied, and (ii) *unsaturated*, which contain one, two or three ethylenic linkages or double bonds. The two types can be represented thus:

Saturated acid - no double bonds



Unsaturated acid



In unsaturated acids containing more than one double bond, the latter may be isolated from each other as in the example preceding, or they may be grouped as closely as possible together and separated by only one C-C linkage. In this case they are said to be 'conjugated'. The following is an acid of this type:



Conjugated unsaturated acid (elaeostearic)

Natural glycerides contain both saturated and unsaturated fatty acids, but it is to the latter that the drying properties are due. The types of fatty acids present in the common drying oils are shown in Table 9.1.

Furthermore, the reactivity and drying properties of conjugated unsaturated acid glycerides is much greater than that of compounds containing isolated double bonds. This accounts for the reactivity of tung oil which contains the conjugated unsaturated elaeostearic acid depicted above.

Drying oils of the linseed type consist of glycerides of fatty acids containing two or three isolated double bonds, whilst semi-drying oils contain acids with only one or two double bonds. This class includes soya bean and tobacco seed oils. Non-drying oils, e.g. castor, consist of glycerides from saturated fatty acids which have no drying properties, or may contain small amounts of acids with one double bond.

The natural vegetable oils rarely consist of pure glycerides, but each glycerol during storage or treatment are due to a rearrangement of acid radicals between the various glycerides.

Again, partial decomposition of glycerides during ripening or processing can lead to the liberation of free fatty acid. The presence and amount of this acid can influence the behaviour of the oil.

The term autoxidation may be encountered in describing these oxidative drying processes. This simply means that atmospheric (gaseous) oxygen is involved and that conditions are mild, compared with other reactions termed oxidations where conditions can involve heat and reactants other than oxygen. During the initial stages of drying, the chief method of cross-linking is by direct combination of free radical sites on different oil molecules. Peroxy, ether and carbon-carbon links can be formed, and chains can be linked as shown below, with ether or C-C links most numerous.

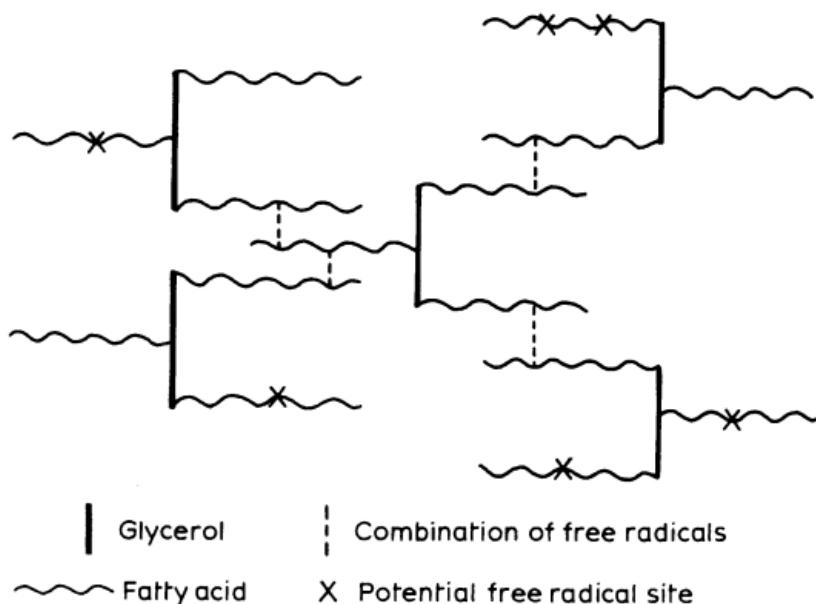
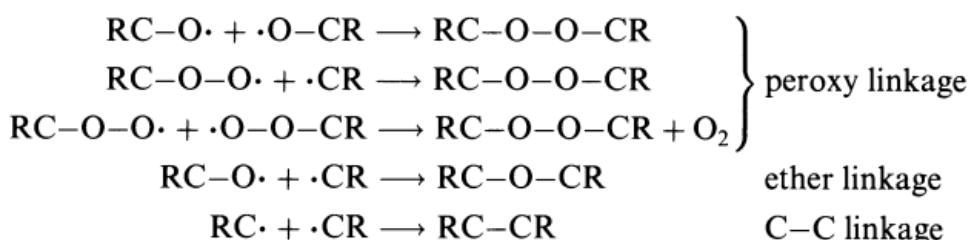


Fig. 12.1 The cross-linking of oil molecules.



Driers

So far the accelerating action of the driers has not been explained. A drier is a metal soap with an acid portion that confers solubility in the oil medium. Synthetic acids, e.g. octanoic (2-ethyl hexoic, $\text{C}_4\text{H}_9 \cdot \text{CH}(\text{C}_2\text{H}_5)\cdot \text{COOH}$), are normally used; naphthenic acids (derivatives of cyclopentane and cyclohexane) formerly used are now rare. Driers are typical additive materials, being present in quantities generally less than 1 %.

Primary driers are true catalysts and contain metals of variable valency, the lower valency being the more stable one, yet capable of oxidation to the higher valency by the products of the drying process. Cobalt and manganese are the principal oxidative driers. The metals act in two ways:

- they promote the uptake of oxygen;
- they catalyse the decomposition of peroxide in free radicals.

The secondary and through driers are of a group of metals, including lead, zirconium, calcium and cerium, which assist the drying of the lower layers of the paint film by mechanisms which

are not fully understood, but probably involve interactions of the metal with carboxyl (and perhaps hydroxyl) groups in the film-former. Because lead is a cumulative poison, permissible levels of lead in household paints have been reduced so much that paint manufacturers now formulate paints of this type without the use of any added lead at all.

In typical air-drying decorative paints, the usual combination now is a mixture of cobalt, calcium and zirconium.

Natural & Synthetic Resins

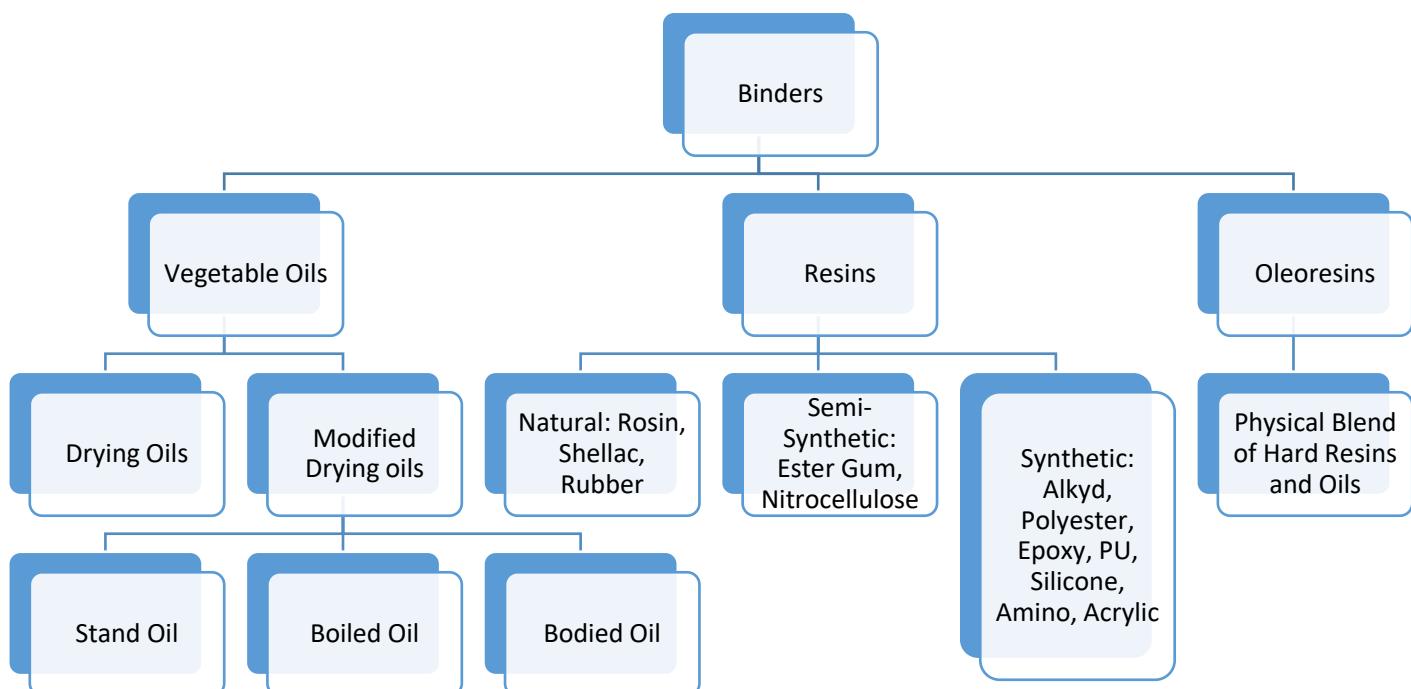
Binder (or film-former)

This is the continuous phase in a paint film and is largely responsible for the protective and general mechanical properties of the film. Film properties depend also on the nature of the pigment, the degree to which the pigment is dispersed in the binder, and the volume of film occupied by the pigment (the 'pigment-volume concentration').

The majority of binders are organic materials – oleoresinous varnishes, resins containing fatty acids from natural oils (alkyds, epoxy esters, urethane oils), treated natural products (cellulose nitrate, chlorinated rubber), and completely synthetic polymers.

A few inorganic binders are used, notably pre-hydrolysed ethyl silicate, quaternary ammonium silicate and alkali silicates (sodium and lithium) which are pigmented with zinc dust to give primers for steelwork.

Organic binders can be divided into two general classes – convertible and



Natural Resins

In the present paint industry natural substances such as resins, plant oil and bitumen are still used. They must be diluted with solvents such as white spirit, xylene, alcohol or acetone. The most important natural resins are rosin, copal, dammar and shellac.

Rosin/Colophony The only natural resin, which plays a noteworthy role in the paint technology. It is extracted from pine trees, together with "turpentine oil. Depending on the method of extraction, two different resin types can be differentiated: the gum resin, obtained by slitting the trunk, and the wood resin, extracted from the rootstock. Colophony is also obtained by the extraction of the so called "tall oil. Colophony consists of different isomers, that means structural versions of the abietic acid. The compact structure explains the solid state of aggregation at room temperature and consequently its resin character. Before employment, colophony has to be "refined" by neutralisation of its acid groups.

Colophony is used as brittle resin in physically as well as in oxidative drying paints. is extracted from pine trees and is diluted in white spirit. This resin has a high acid value and has to be combined with oxides of zinc, magnesium or calcium to neutralise it.

Shellac is the product of the sap of certain trees and is produced by the insect called Laccifer lacca commonly known as the 'lac insect'. This amber coloured resin is soluble in alcohol and can be made water-soluble in combination with amines or ammonia. Resins provide a hard film and are combined with other binders.

Bitumen: Bitumen, asphalt and pitch are dark, hard substances that contain excellent water resistant properties and are used for corrosion protection, roof coatings and vehicle under seals. They are combined with other binders into one and two component products. The use of coal tar is forbidden because it contains toxic polycyclic aromatic hydrocarbons (PAC).

Gilsonite This is one of the most widely used materials of the class and is obtained from North America. It is a lustrous jet-black brittle solid which gives a brown streak when rubbed on paper and breaks down to a brown powder.

Modified natural binders: Modified binders play a big part in natural substances. Cellulose, rubber and fatty acids (plant oils) can be modified to become good binders.

Synthetic Resins

The very wide range of synthetic resins available to both the paint and plastic industries is the result of systematic investigation into the formation of resinous materials, which at one time were regarded as embarrassments in chemical laboratories. Such materials showed no tendency to crystallize and had no sharp melting point. It was realized gradually that these resinous bodies were materials of very high molecular weight and that their formation was associated with the presence of certain groups in the reacting molecules. Furthermore, resin formation depended on the relative quantities of reactants.

Modern synthetic resins are essentially polymers, i.e. they contain large molecules which have been built up from the *normal* molecules or monomers. The number of monomer molecules which go to a given polymer molecule is not constant, so that in a resin there is a range of polymer sizes or molecular weights. These are found to be distributed round a mean value, in much the same way as the particles in a pigment.

There are two general methods for the production of polymers. These are known as *addition* and *condensation* polymerization. The method employed depends on the type of monomer.

Modified binders play a big part in natural substances. Cellulose, rubber and fatty acids (plant oils) can be modified to become good binders.

Fatty acids: alkyds

A combination of “alcohol” and “acid” is called **alkyd**. In chemical terms this reactive product is called **polyester**. The structure of an alkyd consists of oil, alcohol (glycerol) and phtalic acid. More phtalic acid in the alkyd presents a harder and faster drying binder. Increased plant oil in the alkyd results in a weaker and slower drying binder. A high fat-content binder is for exterior application and a low fat-content binder is for interior application.

An alkyd is formed in three steps by

- phtalic acid: $C_6H_4(COOH)_2$, a benzene ring with two acid-groups,
- glycerol: $C_3H_5(OH)_3$, an alcohol with three OH-groups
- carboxylic acid: $R-COOH$, which R is a long chain of linseed oil, that is a mix of linolenic acid, linoleic acid and oleic acid.

There are fatty alkyds containing more than 55 % of plant oil and lean alkyds containing less than 45 % of plant oil. If the alkyd is fatty, the phtalic acid is much less. See Table 3.2.

Figure 3.1: Alkyd molecule structure

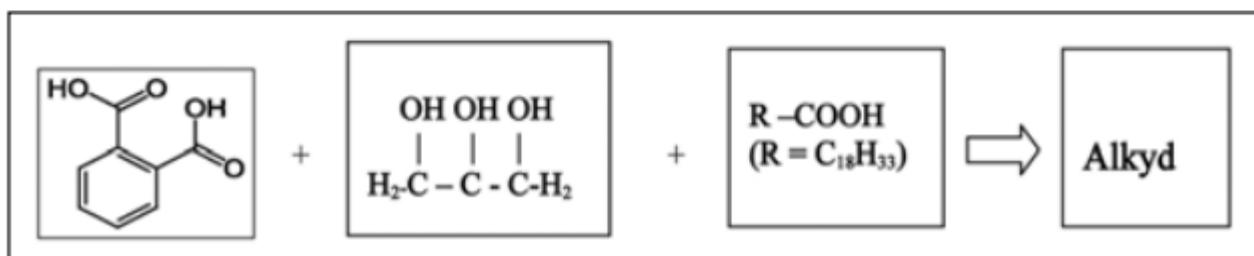


Table 3.2: Types of alkyds

| Types of alkyds | Oil content (%) | PA content (%) |
|------------------------|------------------------|-----------------------|
| Oil free | 0 | 77 |
| Lean | <45 | >40 |
| Medium fatty | 45 to 55 | 30 to 40 |
| Fatty | >55 | 15 to 30 |

If the oil content is high, then the alkyd viscosity is low and the brush ability is good. If the viscosity of a lean alkyd is too high then the brush ability is bad. The thickness of a dried layer from a fatty alkyd is more than the thickness of dried layer from a lean alkyd. The flexibility of a fatty alkyd is higher than that of a lean alkyd. The wet paint film-flow is much better from a fatty alkyd. The yellowing of a dried fatty alkyd paint film is increased compared to a lean alkyd paint film. The durability of a medium fatty alkyd is the best.

Alkyds conforming to the Directive 2004/42/EC (see Chapter 10) have to be composed of more less-solvents. The glycerol changes through an organic alcohol with four or five reactive groups that provide more branching alkyds and better drying time. The low viscosity is attained with shorter oil chains.

The most famous synthetic binder is acrylic which is obtained through a polymerisation process of raw materials from crude oil. This means that a long chain of carbon molecules is built up from the reaction of each molecule together with another molecule. In addition, epoxy and polyurethane binders are now being manufactured.

Acrylic

The acrylic “monomer”, one molecule of pure **acrylate**, comes from the petrochemical industry and can be combined with other monomers. The chemical structure is based on two carbon atoms and carbon acid. A double connection between two carbon atoms is very reactive and can react with other monomers to a polyacrylic

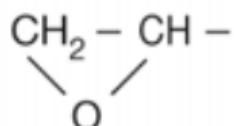


The size of these new molecules is expressed in molecular weight and can range from around 1000 to 3000 g/mol. In practise, it is possible to create many different types of acrylics, such as polyacrylate, methacrylates and styrene acrylates. Each synthetic polymer has a glass transition temperature, which means that the higher the temperature, the harder and less flexible the binder film will be. The glass transition temperature rises as a result of chemical cross-linking. A polymethacrylate has a higher glass transition temperature than a pure polyacrylate.

Acrylic resins are characterised by good chemical and photochemical resistance. This means there is no yellowing and a low UV-degradation in the coating. Acrylics polymers can be solved in solvents and can be dispersed in water (see Chapter 4).

Epoxy

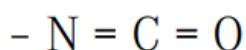
In the organic chemical science there is a special three-member ring resulting from two carbon atoms and one oxygen atom. This is known as the “epoxy group”.



Each epoxy resin has at least two epoxy groups per molecule and is linked to a “bisphenol group”. Bisphenol is composed by two aromatic rings of phenol ($\text{C}_6\text{H}_6\text{-OH}$). Epoxy groups have a tendency to react with amines, so that a two-component product has to be made. Before application both components must be mixed together, after which, the reaction begins immediately. An epoxy reactive molecular group is expressed in equivalent weight (g/mol) and must be linked to the same equivalent weight of an amine for optimal reaction. When too less or too much equivalent weight is present in each component, the remaining component will negatively influence the properties.

Polyurethane

A polyurethane is also a well known polymer based on a chemical reaction from “isocyanate” together with an alcohol-group. An isocyanate group is built up from one nitrogen atom, one carbon atom and one oxygen atom.



This means that polyurethane is a two-component product. Binders contain a lot of the OH-groups. The harder an isocyanate this means it must be mixed before the application. Because an alcohol group resembles a water molecule, polyurethane is also produced as moisture curing quality product. This resin belongs to the one of the component systems. Skin contact with polyisocyanates and especially inhalation of spray mists must be avoided in all circumstances.

The polyurethanes are both thermally and chemically very stable and have a high gloss performance. The first applications, produced by Bayer in Germany, were also used after the Second World War. These coatings are sometimes known as DD coatings, which represent the first two letters of the trade names of Bayer's polymers.

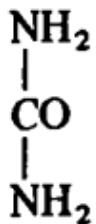
Silicone resins

Silicone resins belong to the class of silicones ($Si = 14$, number in the periodic table (see Appendix 1)) with the scientific name “polysiloxanes” whose characteristic structural feature is the $Si - O - Si$ chain. Many silicones are incompatible to other polymers. Reactive silicones can be linked with alkyds (silicon modified alkyds), polyesters (silicone polyesters) and acrylic resins. The use of silicone resins improves heat resistance, water resistance, surface smoothness and UV retention (gloss maintenance).

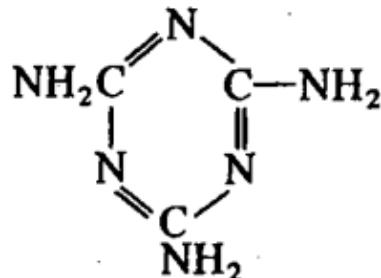
AMINO RESINS

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These are derived by reaction between formaldehyde and either urea or melamine to give urea-formaldehyde or melamine-formaldehyde resins respectively.



Urea
(m.p. 133 C, 271·4 F)



Melamine
(m.p. 350 C, 662 F)

VINYL RESINS

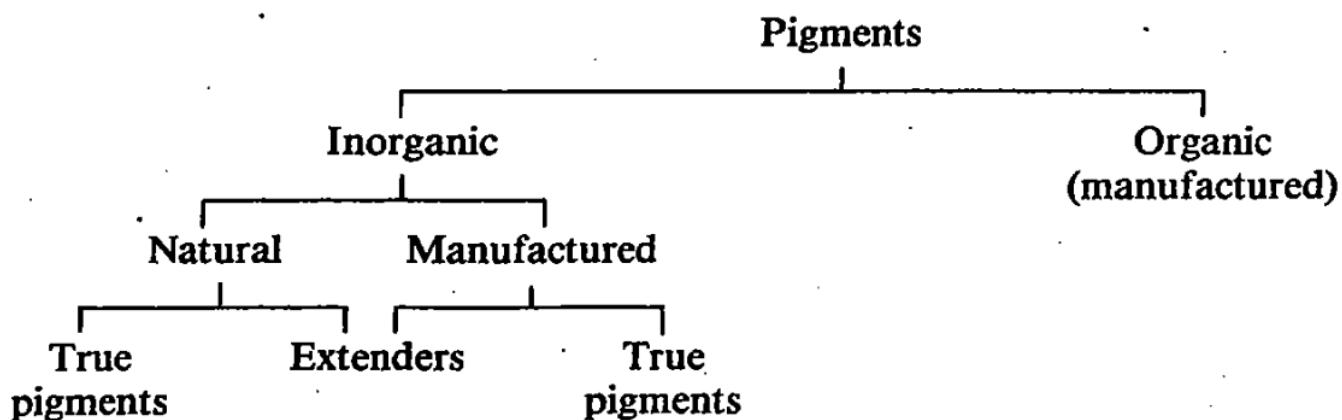
Vinyl resins are straight-chain thermoplastic polymers produced by addition polymerization of compounds containing the vinyl group $\text{CH}_2 = \text{CH}-$. The polymers can be made from straight monomers to give homopolymers or from two or more monomers to give co-polymers. In this way a very large number of co-polymers is possible, for example by polymerizing vinyl acetate with other unsaturated monomers. The polystyrene and acrylic resins are also members of this class.

Pigments and extenders

Pigments are solid particles, insoluble in the resin, solvents used in the paints and capable of being dispersed in the paint constituents to give utmost benefits in terms of the required properties. The physical properties of the pigments such as refractive index and color have profound effects on the aesthetic properties of paint films. Some pigments like Zinc chrome, zinc phosphate etc., are incorporated in the primers for the corrosion protection purpose. Extenders are mainly used in the primers for a wide range of purposes including opacity /obliteration to facilitate sanding. Pigments can be classified into two major classes. The main pigments are added to the formulation, whereas, auxiliary pigments may be added to the paints to provide economic and also modify the reflectance of the coated film (called Gloss). Based on the origin of pigments, it has been further classified as inorganic and organic pigments. The pigments are generally synthetic. Pigments appear in a variety of shapes, including spherical, nodular (rounded but not necessarily spherical), platy (flat or lamellar), acicular (needle-like), fibrous (stringy) or cubic (chunky, block-like lumps). This wide variety of shapes provides the paint formulator with an abundant source of engineering materials for designing or optimizing specific attributes of performance or aesthetics

Pigments

These are finely divided solids, the average particle size of which can vary from 0.2 to 10 μm (micrometres). They may be inorganic or organic in constitution. The general classification of pigments can be illustrated by the following scheme.



Extenders have been included with the inorganic pigments since they are all inorganic solids. They differ from 'true' pigments in their behaviour when dispersed in organic media. True pigments exhibit opacity or hiding power in varying degree, whereas extenders are practically transparent. Extenders are used in certain types of paints (notably undercoats, primers and some low-gloss finishes) to modify or control physical properties. They make no contribution to colour (unless they are very impure) or to opacity.

True pigments are used to provide colour and opacity or hiding power. In finishes they contribute to durability. A pigmented film is more weather-resistant than an unpigmented film of the same binder. In primers for metals, specific pigments are used to check or inhibit corrosion of the metal.

The majority of natural pigments are oxides or hydroxides of iron but may contain appreciable quantities of clay or siliceous matter. The colours are less bright than the corresponding manufactured oxides and hydroxides.

The manufactured inorganic pigments contain the whites and a wide range of colours, including yellows, reds, oranges, greens and blues. Carbon black, consisting essentially of elementary carbon, is usually included in the inorganic pigments.

The organic pigments cover the entire spectrum range, but the brilliance and opacity vary considerably. There are no white organic pigments and organic blacks find only limited use; carbon black satisfies most paint requirements.

In general, organic pigments are brighter than the inorganic counterparts but show much greater variation in opacity and in lightfastness, the latter particularly when mixed with white. Organic pigments derived from plant and animal sources are no longer employed in paint manufacture. Although some possess bright self-colours, they lack permanence. A number which are of historic interest are listed in Appendix C.

Solvents

Solvents are used in paints and lacquers to reduce the viscosity or consistency of the material and so facilitate the application of a uniform coating. They must be solvents that are suitable for the oil or resin present. After application the solvent is no longer required and should evaporate completely from the film.

The resins used in lacquers frequently form hard and brittle films and require plasticizers to confer the necessary elasticity and adhesion. These are usually liquids which must have a minimum tendency to volatilize so that they will remain in the film. It is essential that the plasticizer should be completely miscible with the resin, and to this extent it can be regarded as a solvent.

Paint and lacquer solvents, with the exception of water, are volatile organic liquids which can be classified into well-defined chemical groups. The solvent power and general physical properties vary over a wide range. A useful but arbitrary classification of solvents is by boiling point (though these are not necessarily related to evaporation rates), thus:

| <i>Solvents</i> | <i>Boiling point</i> |
|----------------------|---|
| Low boiling point | Below 100°C (212°F) |
| Medium boiling point | Between 100° and 150°C (212° and 302°F) |
| High boiling point | Between 150° and 250°C (302° and 482°F) |
| Plasticizers | Above 250°C (482°F) |

The important properties of paint solvents are the following:

- 1 Solvent power
- 2 Rate of evaporation
- 3 Boiling point and distillation range
- 4 Flash point and inflammability
- 5 Toxicity.

The following properties are also of importance as indicators of purity—specific gravity, colour, moisture content, acidity or alkalinity, and non-volatile matter.

The solvents more generally used in the surface coatings industry may be divided into three classes:

- (a) hydrocarbon solvents, which consist of carbon and hydrogen only;
- (b) chemical or oxygenated solvents, which consist of carbon, hydrogen and oxygen; and
- (c) water, which consist of hydrogen and oxygen only.

Water is becoming more and more the most important solvent in the paint industry. Water has a very low rate of evaporation and can be mixed with alcohol, ketones and some esters. The surface tension of all binders and solvents varies. Water has a high surface tension (about 70) and white spirit a very low surface tension. Surface tension is determined by cohesive forces and causes the well-known water-drops on fatty surfaces. When ammonia is added to water the drops disappear because the ammonia decreases the cohesive forces. This is the why fatty surfaces need to be cleaned with ammonia or soap products before applying a water-based paint.

PLASTICIZERS

Plasticizers are used in lacquers or non-convertible coatings which dry by solvent evaporation only, and in some types of stoving finish. Their function is to improve flexibility and extensibility of the film without impairing other properties. They should, ideally, be non-volatile, completely compatible with other film components, and chemically stable. The important classes of plasticizers are the following.

Esters

These comprise the largest class. The boiling points of esters increase with increasing molecular weight until the volatility of the material decreases to the point where it can be used as a plasticizer. Esters with boiling points above 250°C (482°F) have, generally, a very low vapour pressure at normal temperatures.

Table 8.2 shows a few of the many ester plasticizers in common use, with their boiling points and the materials for which they are satisfactory plasticizers.

General Formulation of Paint and Basic Machinaries used in its manufacture

The basis of each paint formula is the binder. The binder type and the amount of binder used in a paint formulation decide, for a large part, the paint properties. In Table 6.1, four formulas with different binder percentage of 50, 25, 10 and 5% are mentioned.

The solid content of each formula is calculated and the pigment binder ratio is reproduced. The pigment volume concentration (PVC) is the ratio of the pigment volume to the total volume of the solid coating. In this pigment volume all dry pigments and extenders have been added.

$$\text{PVC} = \frac{\text{Volume Pigments and Extenders}}{\text{Volume Pigments and Extenders} + \text{Volume Binders and resins}} \times 100$$

The volume of the dried film is the sum of all solid binders, resins, plasticisers and additional substances with a solid content.

For calculation of the pigment and binder volume it is necessary to know the densities of the pigments and binders. Generally speaking, the solid binders have a density of 1.2 g/cm³. The pigments and extenders have different densities, for example: titanium dioxide = 4.1g/cm³, carbon black = 1.8 g/cm³, phtalocyanine blue = 1.6 g/cm³, calcium carbonate = 2.8 g/cm³ and iron oxide red = 5.0 g/cm³

Table 6.1: Examples of formula principles

| Paint formulas | Formula 1 strong coating | Formula 2 low solid impregnating | Formula 3 porous coating | Formula 4 low solid colouring |
|----------------------|-----------------------------|-------------------------------------|-----------------------------|----------------------------------|
| Binder (solid) | 50 | 25 | 10 | 5 |
| Pigments/extender | 20 | 5 | 60 | 25 |
| Additives/solvent | 30 | 70 | 30 | 70 |
| Total weight % | 100 | 100 | 100 | 100 |
| Solid content | 71 % | 31 % | 71 % | 31 % |
| Pigment-binder ratio | 1 : 2,5 | 1 : 5 | 6 : 1 | 5 : 1 |
| PVC | 14 | 7 | 71 | 66 |

Dispersion

The next stage is to get the pigment into the paint. The pigment is usually supplied as a powder, in which the granules are actually aggregates of the fine particles produced by the pigment manufacturer. These particles must be dispersed or separated from one another and evenly distributed throughout the paint as a colloidal suspension. For this suspension to have the maximum stability in organic solvents, the surface of each particle should be completely wetted with the varnish; there should be no intervening layers of air or adsorbed water.

Wetting with solvent alone is not enough and pigment dispersions in solvent have poor stability. Each particle in the pigment suspension must be stabilized by polymer chains, anchored to its surface by intermolecular attractions, yet extending out into the varnish because of their attractions for the solvent molecules. When two such particles approach one another, they do not adhere. Contact between them involves the intermingling of polymer chains from the two particles. Locally, in the region between the particles, the concentration of resin molecules is higher than at other points in the paint. This upsets the equilibrium of the system, so solvent molecules diffuse into this region, dilute the concentration and restore

A resin suitable for dispersion usually contains polar groups (which provide the attraction for pigment surface molecules) and is completely soluble in the solvent mixture of the dispersion. Sometimes, surfactants (Chapter 10) are used to bridge the particle–resin interface and assist wetting. In water, ionic surfactants (e.g. soaps) can provide the pigment surface with an electrical charge. The particles, being of like charge, repel one another and the dispersion is stable.

Dispersion is usually carried out in a **mill**, a machine in which the agglomerates are subjected to the forces of shear and (sometimes) attrition. When **shear** is the dispersing action, the agglomerates are squeezed between two surfaces moving in opposite directions, or in the same direction but at different speeds. It is just like making cocoa, where the powder has to be dispersed in a little milk to form a paste. Dispersion is carried out by a shearing motion between spoon and cup. In paint mills the principle is the same, but the power and degree of dispersion are much greater.

During the manufacture of the pigment, the particles are reduced to their ultimate size by crushing or grinding in a liquid slurry, where **impaction** forces are used in a process known as **communition**. Where **attrition** or rubbing forces are part of a dispersion process, the conditions are much milder and there is no attempt to fracture individual particles. In the viscous medium of the varnish, agglomerates – not particles – are broken down.

Several types of mills are used, depending on the difficulty experienced in dispersing the particular pigment. The **high speed disperser** (Fig. 8.2) is used

for easily dispersed pigments and consists of a horizontal disc with a serrated edge (Fig. 8.3), which rotates at high speed about a vertical axis. The dispersion quality may not however be sufficient for full gloss paints. However, pre-dispersion in a high speed disperser may be the preliminary to faster throughput to a sand or bead mill.

The **ball mill** is a cylinder revolving about its axis, the axis being horizontal and the cylinder partly filled with steel or steatite (porcelain) balls, or pebbles. The speed of rotation is such that the balls continually rise with the motion and then cascade down again, crushing and shearing the pigment. Depending on the method of loading, the ball mill can provide actual grinding or size reduction by impaction. This is rarely required, but its ability to provide extreme conditions means that it can be used for the most difficult pigments, such as carbon black. Since grinding times are long, for economic reasons ball mills are only used for these pigments.

In the **sand mill** (Fig. 8.4) or **bead mill**, the axis of rotation may be horizontal or vertical, the grinding medium is coarse sand or beads (glass, zirconia) and the charge is induced to rotate at higher speeds by revolving discs in a stationary container. The ball mill produces a batch of pigment dispersion; the sand grinder gives a continuous output of dispersed pigment. Sand or bead mills in a variety of configurations are now the most frequently used dispersing machinery.

Testing of Paints

Paint test methods are very important for various reasons. In laboratories, during the development of paint, test methods are necessary to assess different proofs. During paint manufacturing test methods are usual for carrying out quality control. Test methods in the paint market are necessary for controlling the correct quality and correct application for the end user.

The paint testing people distinguish between **wet** and **dry** paints.
For the wet paint

- solid content,
- viscosity,
- drying time,
- flow,
- film thickness,
- fineness

are important.

The solid content of wet paint is important for the filling properties and for protection. The viscosity and drying time is also important, such as the dust-free time and the press-free time.

For dried paint, the resistance against water, solvents and chemicals are important tests. Also

- hardness,
- flexibility,
- gloss,
- cleaning,
- hiding power,
- scratch resistance,
- abrasion resistance,
- durability and
- discolouring

Viscosity

Viscosity is a property of a liquid substance and expresses the resistance to forces against which substances can flow. If the ratio between the sheer rate and the sheer stress is constant, the result is an ideal liquid with a maximum flow. This liquid is called “**newtonian**” named after the English scientist

Newton. Examples are: water, solvents and oil. If the ratio between the sheer rate and sheer stress is not constant the liquid is then called “**pseudo plastic**” or “**dilatants**”.



Figure 9.1: Viscosity cup

The Newtonian liquids or paints can be measured with a flow-cup, according to ISO 2431. The content of the cup flows through a hole in the base of the cup within a specific time. Each cup is equipped with different nozzles (holes in mm). The larger the nozzle

Solid content

The solid content of paint provides an indication for filling and protection properties. The non-volatile matter is the residue obtained through evaporation under fixed conditions (ISO 4618). All pigments, extenders, matting agents and binders are solid particles in paint. The solvents, including water, are the volatile components. A small percentage of additives are partly solid and partly volatile. The solid content is a percentage of the total wet paint.

9.2 *Dried properties*

Most measurement tests are carried out on the dried paint film: “the coating”. Primary properties are

- gloss,
- adhesion,
- hardness,
- resistance and
- durability.

However, each application has its own specific properties. Coatings for doors must be scratch resistant and must be able to be cleaned at any time. Coatings for walls must have the same properties, but not in the same range. Exterior window frame coatings must also have the same properties in addition to coatings for toys, garden machinery, computers and oil refineries. The amount of resistance and the resistance to cleaning fluids that are used in the application are just as important. In addition durability varies enormously for numerous paint applications. There are enormous differences between interior and exterior applications and between decorative and industrial applications also.

Gloss

Gloss is measured using reflectometers ISO 2813 by which the angles of incidences can be selected according to the gloss character of the coating film. Directed incident light is reflected by the spread properties of the film. For moderate degrees of gloss (30 to 70 gloss units) the measuring angle is 60° . For high gloss surfaces (more than 70 gloss units at 60° geometry) a 20° measuring angle is recommended. For matt surfaces (under the 30 gloss units at 60° geometry) an 85° measuring angle is advised.

Adhesion

The cross-hatch adhesion test ISO 2409 is performed with a multi-blade knife comprising 10 sharp knives with distances of 1 to 2 mm. With this multi-blade knife a cut in the coating film can be made in a random direction. After that a second cut must be made at the right angle to the first. The adhesion measures are then tested using sticky tape which is pressed onto the hundred block cuts in the coating film and then pulled away. In practice, a knife or sticky tape is often used to scratch or pull a coating film from a substrate.

Application of Paints

The transfer of a liquid paint from container to surface can be effected in a number of ways. Decorative paints are applied by brush or hand roller, but spraying is used on many large exterior surfaces. Both spray and brush application are employed in industrial maintenance painting as, for example, on bridges and other complex structures. A variety of methods are in use in industrial paint application. In the majority of cases these are followed by an accelerated curing operation.

The principal methods of paint application are listed below and later outlined in the text:

| | |
|-----------------|---|
| Brush | Spray – conventional (air-assisted), hot, airless, electrostatic, and combinations |
| Hand roller | Tumbling or barrelling |
| Dip coating | Silk screen |
| Flow coating | Electrodeposition |
| Curtain coating | |
| Roller coating | |

Hand rollers

The roller is made of lamb's-wool or soft plastic foam and is charged with paint by rolling to and fro in a shallow tray with a small quantity of paint. These rollers are very useful for painting large flat areas such as walls, and are popular with home decorators. The soft rollers can be removed easily for cleaning and must be washed out very thoroughly after use, or they will harden and become useless.

Brush application

Brushes are made in many shapes and sizes, ranging from the small round 'pencils' to large flat types. The quality of the bristle is important, and hog bristle has long been regarded as the finest type. The bristles subdivide and so produce a number of fine ends which help to minimize brush-marking in the film. Nylon bristles also are used; these are more wear-resistant than the animal bristles.

New brushes are usually *broken in* by use with primers. Brush application is the most satisfactory method of applying primers to most surfaces as the paint can be 'scrubbed' in, giving good wetting and adhesion. The scrubbing action, however, must be avoided in the application of undercoats and finishes. With these, the paint is applied more liberally and with longer strokes, cross-brushed, and finally *laid off* with light strokes across the surface.

After use, paint brushes should be cleaned in white spirit or other suitable solvent and stored suspended by the handle so that they do not rest on the

SPRAY METHODS

Conventional spray application

The general principle in spray application is atomization of the paint into a fine spray which is directed on to the object. A number of methods have been devised to perform this, and the earliest was the use of compressed air with a spray gun.

Spray guns

For small-scale work the paint is contained either in a cup fitted on top of the spray gun so that the paint feed is by gravity, or in a cup below the gun, from which the paint is drawn by suction. These guns are very useful if frequent colour changes are involved.

For large-scale and production work a continuous supply of paint to the gun is required. The paint is contained in a pressure vessel connected to compressed air and fed to the gun through pressure hose. A cut-away section of this type of gun is illustrated in Fig. 20.2. The paint leaves the needle valve and is mixed with the compressed air from jets surrounding the valve. Mixing of the paint and air can take place either outside or inside the tip of the gun, and this is determined by choice of gun fittings appropriate to the type of paint to be sprayed. A trigger mechanism controls both paint flow and compressed air and is arranged so that the air flow precedes the paint.

THE END
