PAINTS AND PIGMENTS

What are Paints:

Paints are stable mechanical mixtures of one or more pigments. The main function of the pigments is to impart the desired colour and to protect the paint film from penetrating radiation, such as U.V. rays. The pigments and the extenders are suspended in drying oils called **vehicle.** The vehicle or drying oil is a film forming material, to which other ingredients are added in varying amounts. The paint is applied on a metal or wood surface to give it a protective coating. **Driers** promote the process of film formation and hardening. **Thinners** maintain the uniformity of the film by reducing viscosity of the blend. The important varieties of paints are emulsion paints, latex paints, metallic paints, epoxide resin paints, oil paints, water paints or distempers, etc.

Composion of Paints:

A paint is formulated as a mixture of four ingredients:

- **Binder**
- **Solvent**
- **Pigment**
- **Additives**

Binders:

Binder is the main ingredient of paints. Binders are polymers (resins) forming a continuous film on the substrate surface. Binders are responsible for good adhesion of the coating to the substrate. The binder holds the pigment particles distributed throughout the coating. The binder is dispersed in a carrier (water or organic solvent either in molecular form (true solutions) or as colloidal dispersions (emulsions or sols). Common binders are as follows:

- **Alkyd resins** are prepared by the condensation polymerization in the reaction of fatty acid and polyols (commonly glycerol) with polybasic acids.
- **Acrylic resins** are prepared by polymerization of acrylic or methacrylic esters.
- **Latex (PVA)** is a vinyl polymer prepared by free radical vinyl polymerization of the monomer vinyl acetate.
- **Phenolic resins** are thermosetting polymers prepared by the reaction of simple phenol with aldehydes (eg. formaldehyde).
- **Urethane resins (polyurethanes)** are prepared by the step-growth polymerization of isocyanates reacting with monomer molecules containing hydroxyl (alcohol) groups.
- **Epoxy resins** is a thermosetting polymer formed as a result of cross-linking a resin containing short molecules in the presence of a hardener.

- **Chlorinated rubber** is prepared through polymerization of the degraded natural rubber (in the presence of atoms of chlorine participating in cross-linking.

Solvents of paints:

Solvent (water or organic solvent) is a medium where the binder, pigment and additives are dispersed in molecular form (true solutions) or as colloidal dispersions (emulsions or sols).

Solvents (thinners) are also used for modification of the paint viscosity required for the application methods: brush, roller, dip, spray.

The solid coating is formed due to evaporation of solvent therefore the evaporation rate is one of the important properties of solvents. Other important properties are the ability to dissolve the paint ingredients and toxicity.
The solvents used as the carrier in paints:

- **Water**
- **White spirits (mineral turpentine spirits)**. White spirit is a mixture of is a mixture of saturated aliphatic and alicyclic hydrocarbons.
- **Xylene** is a pure aromatic solvent having benzene ring structure in its molecule (C_8H_{10}).
- **Toluene** is also a pure aromatic solvent with benzene ring structure ($C_6H_5CH_3$).
- **Alcohols (n-butanol, isopropanol)** are organic compounds having a hydroxyl groups (-OH) bound to the carbon atoms of an alkyl group.
- **Ketones** is an organic solvents, in which carbonyl group (C=O) is bonded to two other carbon atoms.

Pigments of paints:

Pigment is a solid substance dispersed throughout the coating to impart it a color, opacity (hide the substrate surface). Pigments may protect the substrate from UV light. Pigments change the paint appearance (gloss level) and properties: increase hardness and decrease ductility. Pigments may be natural, synthetic, inorganic or organic. Fillers and extenders are also referred to pigments. **Fillers and extenders** are non-expensive commonly natural inorganic materials added to the paint in order to increase its volume, to increase the paint film thickness, to impart toughness or abrasion resistance to the coating. Pigments commonly used in paints:

White pigments

Pigments that contribute light-scattering properties to coatings are generally known as white, or hiding, pigments. They act by scattering all wavelengths of light, owing to their relatively high refractive index, so that they are perceived as white by the human eye. They are known as hiding pigments because the scattering of light reduces the probability that light will penetrate through a pigmented film to the substrate. A paint film of sufficient thickness and concentration of light-scattering pigment is truly opaque, hiding the substrate. The whiteness and opacity contributed by this class of pigments make them among the most extensively used pigments for coatings.

- **Titanium Dioxide** (TiO_2): The most widely used white pigment is the crystal form of titanium dioxide (TiO_2) known as rutile. Rutile has the highest index of refraction (2.76) of any material that can be manufactured in pigment form at a reasonable cost, making it the most efficient white pigment available. Another crystal form of TiO_2, anatase, is sometimes used in coatings, but its lower index of refraction (2.55) makes it a less optically efficient pigment. Furthermore, surface-treated TiO_2 in its rutile form yields coatings that are more durable to exterior exposure than are equivalent anatase pigments. TiO_2 pigments are used in very high volume worldwide, especially in the so-called trade sales market, which includes retail, architectural, and contractor markets. In these applications, light, pastel, and white coatings predominate—thus the demand for TiO_2.
- Other **white pigments** are zinc oxide (ZnO), zinc sulfide (ZnS), and lithopone, a mixture of barium sulfate ($BaSO_4$) and ZnS. The earliest commercial white pigment was "white lead," basic lead carbonate ($2PbCO_3 \cdot Pb[OH]_2$), which was widely used until about 1925–30. Because of this compound's solubility in water, it is a toxic hazard, and its use in coatings has been restricted since the 1960s. Its commercial use actually stopped much earlier; because of its low index of refraction (1.94), white lead had been replaced by titanium dioxide, which is more than eight times as efficient in hiding power. Nevertheless, the presence of old, peeling paint containing white lead pigment continues to be a health hazard in older buildings that are poorly maintained.

Coloured pigments

Coloured pigments fall into two main groups, inorganic pigments and organic pigments. As a result of legislation governing the handling and use of toxic materials, many of the inorganic pigments traditionally used by the paint industry have been replaced by other less toxic materials. Thus except in a few industrial compositions lead pigments of all types (e.g. chromate, oxide, carbonate) have to a large extent been replaced, and it is to be expected that lead in all of its forms and chromates will ultimately be eliminated from all paints. Their removal from the scene gives rise to problems if a coloured pigment is used for the dual purposes of providing colour and contributing positively to the anti-corrosive properties of the paint film.

Some commonly used pigments are shown in the following Table.

Some commonly used pigments:

Colour	Inorganic	Organic
Black	Carbon black Copper carbonate Manganese dioxide	Aniline black
Yellow	Lead, zinc, and barium chromates Cadmium sulphide Iron oxides	Nickel azo yellow
Blue/violet	Ultramarine Prussian blue Cobalt blue	Phthalocyanin blue Indanthrone blue Carbazol violet
Green	Chromium oxide	Phthalocyanin green
Red	Red iron oxide Cadmium selenide Red lead Chrome red	Toluidine red Quinacridones
White	Titanium dioxide Zinc oxide Antimony oxide Lead carbonate (basic)	—

- **Zinc Yellow (Yellow 36)** is Zinc Chromate ($ZnCrO_4$).
- **Yellow Dyes** are stable yellow non-toxic organic pigments with good opacity.
- **Benzidine Yellows** are yellow-to-red organic pigments for interior applications. They are resistant in chemicals and stable at elevated temperatures (up to 300°F / 150°C).
- **Chrome Oxide Green** is olive-green inorganic pigment with a high level of opacity. Chrome Oxide Green is the most stable green pigment.
- **Phthalocyanine Green** imparts green-blue color. It is used as the pigment for decorative applications. The pigment is resistant to heat, solvents and alkalis.
- **Phthalocyanine Blues** are widely spread pigments. They provides a wide spectrum of color: from reddish-blue to yellowish-green. The pigments are non-toxic and resistant to solvents, chemicals and elevated temperatures.
- **Ultramarine Blue** is natural pigment made of the semiprecious mineral lapislazuri. The pigment is resistant to fading. It is stable at elevated temperatures.
- **Vermilion** is a natural orangish red pigment consisting of toxic mercuric sulfide (HgS).
- **Pigment Brown 6** is red inorganic pigment based on Iron(III) oxide (Fe_2O_3).
- **Red 170** is a synthetic organic pigment widely used in automotive industry.
- **Dioxazine Violet** is organic synthetic pigment.It is non-toxic and has high tinting strength.

- **Carbon Black** is the pigment obtained from organic materials (wood, bones) by charring (thermal decomposition in a limited amount of Oxygen). large quantities of Carbon Black are used for coloring and reinforcing automobile tires.
- **Iron (II) Oxide (FeO)** is inorganic black pigment.

Examples of fillers and extenders:

The extenders or fillers are the low cost materials. These are added to the paint in order to decrease the cost of the paint. These supplement the pigment in increasing the covering and weathering power of the film. Filler pigments are differentiated from other pigments in that they usually have little or no effect on the coatings' optical properties other than gloss. Examples of the materials used as filler pigments are:

- **Quartz sand (SiO_2)**. Finely ground quartz is a filler increasing the abrasion resistance of the paints.
- **Talc** having the lamellar structure serves as a reinforcing phase in the coating. Talc also protects the substrate from the penetrating water.
- **Baryte ($BaSO_4$)** is a colorless or white inorganic mineral having high hardness and chemical resistance. It is used as a reinforcing additive.
- **Kaoline Clay** is a natural colloid containing finely dispersed particles of hydrated aluminum silicate. Kaoline Clay is used in emulsion paints as a gloss reducing additive.
- **Limestone** (calcium carbonate, $CaCO_3$) is used in emulsion paints as a filler extending expensive pigments.

<u>Additives for paints:</u>

Additives are small amounts of substances modifying the paint properties. Examples of additives:

- **Driers: Driers** (which are oxygen carriers) have also been used in the paints, in order toaccelerate the drying of the film through oxidation and polymerization. Earlier, PbO was used as a drier, but the **Modern driers** are Co, Mn, Pb, Zn, resinoleate, linoleate and naphthenates, etc.
- **Catalyst**: Another key component of coatings used at low concentrations are the catalysts and driers that help to accelerate film-formation reactions. The earliest catalysts for curing were discovered by accident, when it was determined that the presence of lead oxide pigments such as red lead caused oil-based coatings to cure more rapidly and thoroughly than in their absence. The reactive species that causes this reaction is the Pb^{2+} ion, which forms organic salts with the fatty acid components of the drying oil. The lead–fatty-acid salt catalyzes the decomposition of organic hydroperoxides formed by the interaction of oxygen from the air with the unsaturated fatty acids in the drying oils. In turn, the free-radical decomposition products of the hydroperoxides cause the chain reactions known as oil drying. Lead-based pigments and driers are now unavailable because of their toxicity, but other organometallic driers, such as cobalt and zirconium naphthenate, are commonly used in alkyd and oil-based coatings.

Most cross-linking reactions, such as polyol-polyisocyanate reactions that take place during the formation of polyurethane coatings, are also catalyzed. In this reaction class, dibutyltin dilaurate (DBTDL) is often used as a reaction catalyst to accelerate the urethane reaction. Other cross-linking reactions have specific catalysts that provide sufficient reaction acceleration to allow film formation in a reasonable amount of time after application.

- **Wetting agents**: In both the production and the application of coatings, the wetting of solid surfaces by the fluid phase is necessary. Chemicals that alter the surface properties of the coating fluid and reduce its surface tension are known as wetting agents. (In actuality, these materials are very similar to those used in dishwashing liquids, hand soaps, and shampoos and are identified under the general heading of surfactants.) Wetting agents help the fluid phase to wet pigment particles during the pigment-dispersion process (see below), and they also help to reduce the surface tension of the coating so that it properly wets the substrate upon application**.**
- **Thinners or Diluents:** Another ingredient, of paint is **thinner**. It is added to the paints to dissolve film forming materials and to dilute concentrated paints for better handling. After adding thinner, the paints may be applied more easily on the surface by brushing, spraying or dipping. **Mineral spirits** and solvents namely **turpentine**, maintains the fluidity of the freshly applied film for reasonable period of time.
- **Plasticisers** increase the paints flexibility. **Plasticizers** are added to the paints to provide elasticity to the film and thus prevent cracking of the paint. Chemically, plasticizers are mostly esters. Triphenyl Phosphate, dibutyl phthalate and castor oil etc. are used as **Plasticizers.**
- **Fungicides, Biocides and Insecticides** prevent growth and attack of fungi, bacteria and insects. In order to stabilize aqueous latex coatings for long-term storage, bactericides are often added. Similarly, latex coatings for exterior architectural use often contain fungicides that help to prevent the formation of mildew on exterior surfaces. Also, most water-based coatings require pH-control agents. When hard water is used in the manufacture of coatings, sequestrants (additives that prevent precipitation reactions) such as tetrapotassium pyrophosphate are utilized to help stabilize the coating. For latex coatings that are stored in garages in cold in automobile antifreeze, are used to provide freeze-thaw stability.
- **Flow control agents** improve flow properties.
- **Defoamers:** One problem with specialty additives is that they often have a surfactant nature and consequently stabilize foam in the liquid coating. Portions of the coating polymer also have a surfactant nature, and they, too, contribute to foam stability. Foam often causes problems during manufacture and packaging, and during application it often causes film defects such as bubbles and subsequent thin spots. In order to counteract this problem, defoamers—materials that destabilize or break foams—are often added to coatings. Defoamer activity is not yet completely understood, but the agents seem to act

by destabilizing the surface films of bubbles or by spontaneously spreading on the surface of these films as they form and breaking the bubbles. Defoamers are often based on silicone oils with fine silica particles added as a carrier for the silicone.

- **Emulsifiers** are wetting agents increasing the colloidal stability of the paints in liquid state. Examples of emulsifiers include sodium phosphates, sodium stearoyl lactylate, soy lecithin, Pickering stabilization, and DATEM (diacetyl tartaric acid ester of monoglyceride).
- **UV stabilizers** provide stability of the paints under ultra-violet light.
- **Anti-skinning agents:** Certain **antiskinning agents** are also added to the paints in order to prevent gelling and skinning of the finished product before application of the paints by brushing, spraying or dipping. Polyhydroxy phenols are usually employed as **antiskinning agents.**
- **Adhesion promoters** improve the adhesion of the coating to the substrate.
- **Corrosion inhibitors** reduce the corrosion rate of the substrate.
- **Texturizers** impart textures to the coatings.