

# Unit-V: Surface Chemistry & Surface Coatings

## **UNIT- V Surface Chemistry and Surface Coatings**

**(10 Hours)**

Adsorption-Types of adsorption-adsorption of gases on solids- adsorption from solutions- Types of isotherms Freundlich adsorption isotherm, Langmuir adsorption isotherm. Industrial applications of adsorption. Surface Coatings Objectives of coatings surfaces, preliminary treatment of surface, classification of surface coatings. Paints and pigments- formulation, composition and related properties. Oil paint, Vehicle, modified oils, Pigments, toners and lakes pigments, Fillers, Thinners, Enamels, emulsifying agents. Special paints (Heat retardant, Fire retardant, Eco-friendly paint, Plastic paint), Dyes, Wax polishing, Water and Oil paints, additives, Metallic coatings (electrolytic and electroless), metal spraying and anodizing.

# Langmuir Adsorption Isotherm

# Applications of Adsorption

## 5 APPLICATIONS OF ADSORPTION

(1) *Activated charcoal is used in gas masks* in which all undesirable (toxic) gases are adsorbed selectively by charcoal; while purified air passes through its pores.

(2) *Activated charcoal is used for removing colouring matter of sugar solution and the decoloration of vinegar.*

(3) *Silica and alumina gels are used as absorbent for removing moisture and for controlling humidities of room.* Silica gel has been employed for drying air, used in blast furnaces.

(4) *Charcoal adsorption filters are used for removing organic matter from drinking water.*

(5) Selective adsorption by alumina, magnesia, etc., has been used for separating different pigments by adsorption chromatography.

(6) *During arsenic poisoning, colloidal ferric hydroxide is administered.* The latter adsorbs the arsenic poison and retains it and can thus be removed from the body by vomiting.

(7) *Fuller's earth* is used in large quantities for refining petroleum and vegetable oils, due to its good adsorption capacity for unwanted materials.

(8) The phenomenon of adsorption is useful in heterogeneous catalysis, e.g., contact process, Haber's process, hydrogenation of oils, etc. based on adsorption process.

(9) Adsorption process is used in *production of vacuum* by using activated charcoal in Dewar's flask.

(10) *Lake test for  $Al^{3+}$*  is based upon adsorption of litmus colour by  $Al(OH)_3$  precipitate.

(11) *Mordants* (like alum) used in dyeing cloth, adsorb the dye particles, which otherwise do not stick to the cloth.

# **Surface Coatings (Protective Coatings)**

## 10 ORGANIC COATINGS

*Organic coatings are inert organic-barriers (like paints, varnishes, lacquers and enamels) applied on metallic surfaces and other constructional materials for both corrosion protection and decoration. The protective value of such a coating depends on : (i) its chemical inertness to the corrosive environment, (ii) its good surface adhesion, (iii) its impermeability to water, salts and gases, as well as (iv) its proper application method.*

## ✓ 11 PAINTS

*Paint is a mechanical dispersion mixture of one or more pigments in a vehicle. The 'vehicle' is a liquid, consisting of non-volatile, film-forming material, drying oil and a highly volatile solvent, thinner. When a paint is applied to a metal surface (usually by brushing or spraying), the thinner evaporates ; while the drying oil slowly oxidizes forming a dry pigmented-film.*

**Requisites of a good paint :** A good paint possesses the following characteristics : (1) It should be *fluid enough* to be spread easily over the protected surface. (2) It should possess *high covering power*. (3) It should form a *quite tough, uniform, adherent and impervious* film. (4) Its film should *not get cracked on drying*. (5) It should *protect the painted surface from corrosion effects of environment*. (6) It should form film, *the colour of which is quite stable* to the effect of atmosphere and other agencies. (7) Its film should be *glossy (i.e., having shine or luster)*. (8) Its film should be *stable*. (9) It can be prepared in such a consistency as to be *easily applicable* with brush or spraying device and that it yields a *smooth and uniform surface*. (10) It should possess *high adhesion capacity* to the material over which it is intended to be used.

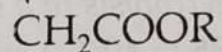
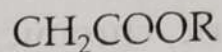


**Constituents of paints : 1. Pigment** is a solid substance, which is an essential constituent of paint. Its functions are to : (i) provide capacity to paint, (ii) provide strength to paint, (iii) provide desired colour to paint, (iv) give aesthetical appeal (i.e., pleasing to look at) to the paint film, (v) give protection to the paint film by reflecting harmful ultraviolet light, (vi) provide resistance to paint film against abrasion/wear, (vii) improve the impermeability of paint film to moisture, and (viii) increase weather-resistance of the film.

Pigments used *whites* [such as white lead, zinc oxide, lithophone, titanium oxide] or coloured [(i) red—red lead, ferric oxide, venetian red, chrome red, (ii) green—chromium oxide, (iii) blue—prussian blue, (iv) black—carbon black, (v) brown—brown umbre, etc].

**Characteristics of good pigments** : Good pigments should be : (i) opaque, (ii) chemically inert so that paint film has stability and longer life, (iii) non-toxic so that there is no bad effect on the health of painter as well as inhabitants, (iv) freely mixable with film-forming constituent, oil, and (v) cheap.

**2. Vehicle or drying oil** is a film-forming constituent of the paint. These are glyceryl esters of high molecular-weight fatty acids, generally, present in animal and vegetable oils.



The most widely used drying oil, are linseed oil, soyabean oil, and dehydrated castor oil.

**Table 4.** Fatty acids present in oils and fats.

<i>Name of acid</i>	<i>Formula</i>	<i>Position of unsaturation (if any)</i>
Caproic	$C_5H_{11}COOH$	Saturated
Caprylic	$C_7H_{15}COOH$	Saturated
Capric	$C_9H_{19}COOH$	Saturated
Lauric	$C_{11}H_{23}COOH$	Saturated
Myristic	$C_{13}H_{27}COOH$	Saturated
Palmitic	$C_{15}H_{31}COOH$	Saturated
Stearic	$C_{17}H_{35}COOH$	Saturated
Arachidic	$C_{19}H_{39}COOH$	Saturated
Behenic	$C_{21}H_{43}COOH$	Saturated
Lignoceric	$C_{23}H_{47}COOH$	Saturated
Cerotic	$C_{25}H_{51}COOH$	Saturated
Oleic	$C_{17}H_{33}COOH$	Unsaturated 9th carbon atom
Linoleic	$C_{17}H_{31}COOH$	6th and 9th carbon atoms ( <i>two</i> double bonds)
Linolenic	$C_{17}H_{29}COOH$	3rd, 6th and 7th carbon atoms ( <i>three</i> double bonds)
Eleostearic	$C_{17}H_{29}COOH$	5th, 7th and 9th carbon atoms ( <i>three</i> double bonds)



**Notes :** (1) **Drying oil** are oils containing **high** percentage of conjugated fatty acid esters, and they dry quickly by absorbing oxygen (from air) to adherent, horn-like solid substances. They are used in paint. For example, linseed oil, tung oil, perilla oil, dehydrated castor oil, oiticia oil, etc.

(2) **Semi-drying oils** are oils containing **low** percentage of conjugated fatty acid esters or high percentage of unsaturated fatty acid esters containing one double bond only. They dry very slowly in air and are not used in paints as such. However, they are used as blending agent with other drying oils to get desired film on drying. Examples are soyabean oil, rosin oil, fish oil, etc.

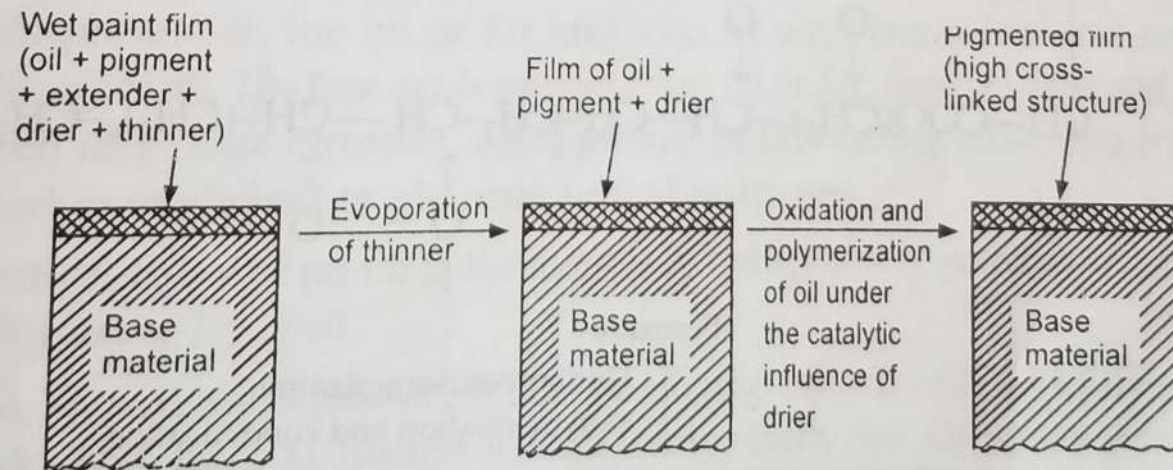
(3) **Non-drying oil** are oils containing **only saturated** fatty acid esters. They do not dry at all, even on long exposure to air. For example, mustard oil, sunflower oil, rapeseed oil, etc.

**Table 5 :** Drying oils versus semi-drying oil.

Drying oils	Semi-drying oils
1. They dry <i>quickly</i> in air to form adherent, and horn-like films.	They dry <i>very slowly</i> in air.
2. They are composed of <i>high</i> percentage of conjugated fatty acid esters of glycerol.	They are composed of <i>low</i> percentage of conjugated fatty acid esters or high percentage of single double bond containing fatty esters of glycerol.
3. They are used in <i>paints</i> .	They are used as <i>blending agent</i> with drying oils in paints.
4. Linseed oil, tung oil, perilla oil, etc. are examples.	Soyabean oil, rosin oil, fish oil, etc. are examples.

**Functions of drying oils :** Drying oil supplies to paint-film : (i) main film-forming constituent, (ii) vehicle or medium, (iii) toughness, (iv) adhesion, (v) durability, and (vi) water-proofness.

**Reactions in drying of oils :** The oil film, after it has been applied on the protected surface, absorbs oxygen (of the air) at the **double bonds**, forming peroxides, diperoxides and hydroperoxides, which isomerise, polymerize and condense to form a characteristic tough, coherent, hard, elastic, insoluble, infusible, highly cross-linked structured macromolecular film. The final hardened product actually resembles a thermosetting resin in chemical structure (see next page for equations).

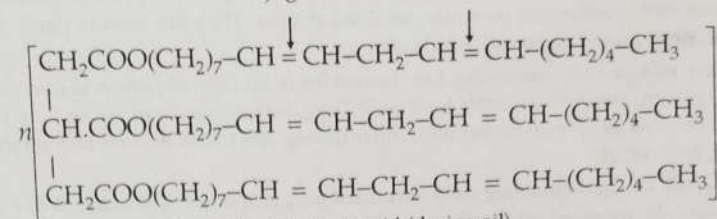


**Fig. 4.** Drying of a paint film.

3. **Thinners** : (i) *reduce the viscosity* of the paint to suitable consistency, so that it can easily be handled and applied ; (ii) *dissolve vehicle* and the additives in the vehicle ; (iii) *suspend the pigments* ; (iv) *increase the penetration power* of the vehicle ; (v) *increase the elasticity* of the paint film; (vi) *help the drying* of the paint film, as they evaporate.

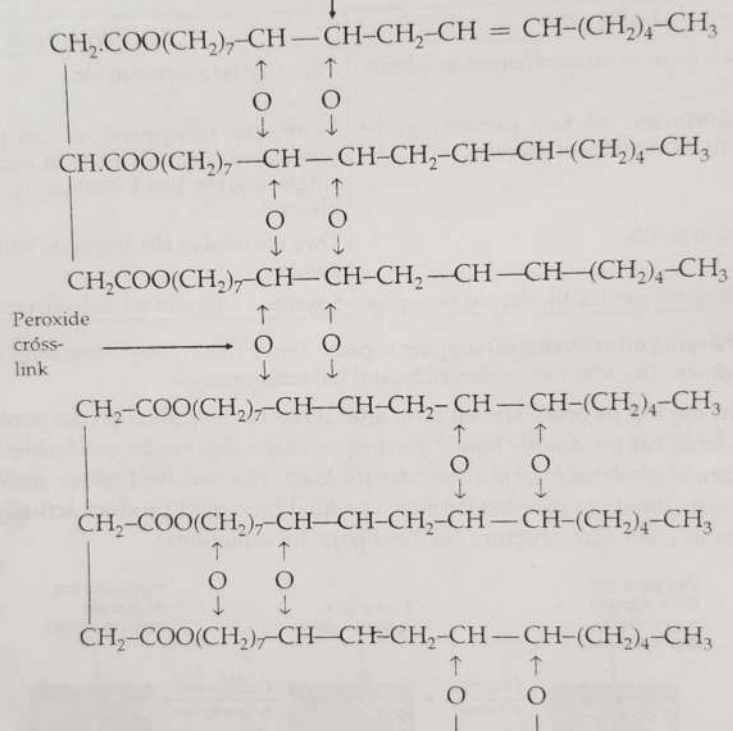
Common thinners used are *turpentine* (produced by the distillation of a resinous exudation of some kind of pine trees), *mineral spirits* (from petroleum), *benzene*, *dipentene*, *naphtha*, *toluol*, *xylol*, *kerosene*, *methyalted naphthalene*, etc.

Conjugated double bonds



- Glyceride of linolenic acid (drying oil)

Air oxidation and polymerization



Peroxide

Undergoes isomerization,  
polymerization and condensation

Highly cross-linked structured  
macromolecular film



**4. Driers** are oxygen-carrier catalysts. They accelerate the drying of the oil-film through oxidation, polymerization and condensation. Thus, their main function is to improve the drying quality of the oil-film.

The most effective driers are resinates, linoleates, tungstates and naphthenates of Co, Mn, Pb and Zn. (i) Cobalt substances are the most efficient of all and are 'surface-driers'. (ii) Lead substances are 'bottom-driers'; while (iii) manganese substances are 'thorough-driers'. Too much of a drier tends to produce hard and brittle films.



**5. Extenders or fillers** are low refractive indices materials, generally, of white colour, added to :

(i) reduced the cost, (ii) increase durability of the paint, (iii) provide negligible covering power to the paint, (iv) help to reduce the cracking of dry paint film and sometimes help to keep the pigments in suspension, (v) serve to fill voids in the film, (vi) increase random arrangement of pigment particles, and (vii) act as carriers for the pigment colour.

Important extenders used are barytes ( $\text{BaSO}_4$ ), talc, asbestos, ground silica, gypsum, ground mica, slate powder, china-clay, whiting ( $\text{CaCO}_3$ ), magnesium silicate, diatomite clay, calcium sulphate, etc.

**6. Plasticizers** : Sometimes, plasticizers are incorporated in the paint : (i) to provide elasticity to the film, and also (ii) to minimize its cracking. Common plasticizers used are tricresyl phosphate, triphenyl phosphate, tributyl phthalate, diamyl phthalate and dibutyl tartarate.

**7. Antiskinning agents** are, sometimes, added to some paints with the object of preventing gelling and skinning of the paint film. Important antiskinning agents are polyhydroxy phenols.

### 13 FORMULATION OF PAINTS

Manufacture of paints depend upon proper composition of paint to meet the specific requirements. These requirements may be listed as : (1) *hiding power*, (2) *colour fastness*, (3) *weather-resistance*, and (4) *consistency (for proper application)*. These requirements are met by proper choice of pigments, vehicles and extenders by the paint formulator. The most important concept for a modern paint formulator is :

**Pigment volume concentration (P.V.C.)**, which is the concentration by *volume* of the pigments expressed as a percentage of the total volume of non-volatile constituents of the paint. As non-volatile volume in paint is the sum of the volumes of pigment and non-volatile vehicle, therefore., P.V.C. can be express mathematically as follows :

$$\text{P.V.C.} = \frac{\text{Volume of pigment in paint}}{\text{Total volume of non-volatile constituents of the paint}}$$

$$= \frac{\text{Volume of pigment in paint}}{\text{Volume of [pigment + non -volatile vehicle] constituents of the paint}}$$

**Importance of P.V.C. :** The P.V.C. largely controls such factors as gloss, washability, adhesion and durability. Thus :

- (1) When the P.V.C. is increased, the gloss decreases, until paint becomes flat.
- (2) With the increase in P.V.C., the relative quantity of binder decreases, therefore, the film-formed loses cohesion and hence, durability. So, with the increase in P.V.C., the adhesion and durability of paint-film decreases.
- (3) With the increase in P.V.C., the washability of paint-film decreases.
- (4) Extnders, when added to a paint, amounts to increase in P.V.C., and thus, decrease the gloss, washability, durability and adhesion. So, in case the pigment is costly and its covering power is high, a portion of the pigment may economically be replaced by extenders, without sacrificing the covering power of pigment.
- (5) Opacity of white paint is created by the difference in the refractive indices of the pigment and vehicle. It is also influenced by the 'size' of the dispersed pigment particles and P.V.C.



## 14 FAILURE OF A PAINT FILM

A paint is considered as failed in the following cases :

1. **Chalking** is the progressive powdering of the paint film on the painted surface. This occurs due to improper dispersion of pigment in vehicle or by destruction of binder by the continuous exposure to light.
2. **Flaking** is peeling of the paint film from the painted surface. This is due to the presence of dust particles or greasy matters in the paint. These foreign matters result in poor adhesion of the paint to the painted surface.
3. **Cracking** of paint film is due to the unequal expansion or contraction of different coats of the paint, caused by variation of the temperature of the exposed film. This defect can, however, be prevented by making the first coat (or primary coat) a harder one.
4. **Colour change of the paint film** after some time is due to the chemical effect of atmospheric gases on the paint. For example, white lead-containing paint film *tarnishes* (i.e., turns blackish), when exposed to atmosphere, containing sulphur-containing gases (like  $H_2S$ ). Similarly, zinc oxide-containing paint film becomes yellow.

The paint failure can be **prevented** by : (1) Scientific mixing and proportioning of the ingredients of proper characteristics. (2) Using only suitable and selected paint for a particular job. (3) Preparing carefully the surface, before application of paint. (4) Applying a suitable primer-coat. (5) Properly applying the paint evenly. (6) Allowing each paint coat to dry sufficiently, before the newer/next coat is applied.

## 15 VARNISHES

**Varnish** is a homogeneous colloidal dispersion-solution of natural or synthetic resin in oil or thinner or both. It is used as a protective and/or decorative coating of suitable surfaces and dries by evaporation, oxidation and polymerization of its constituents ; leaving behind a hard, transparent, glossy, lustrous and durable film. There are two main types of varnishes :

(1) **Oil varnish (or oleoresinous varnish)** is a homogeneous solution of one or more natural or synthetic resins in a drying oil and a volatile solvent. The presence of oil **reduces the natural brittleness**

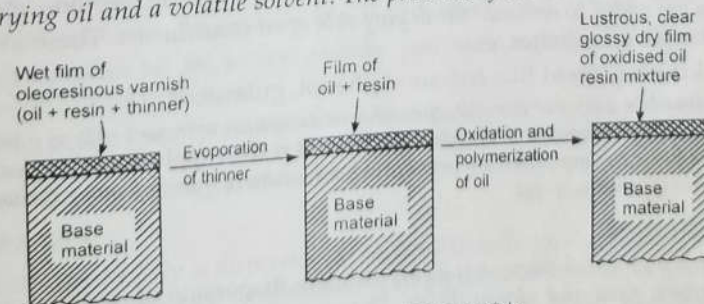


Fig. 5. Drying of an oleoresinous varnish.



**Characteristics of a good varnish :** A good varnish should possess the following characteristics. It should : (1) be soft and tender ; (2) adapt itself to the contraction/expansion of coated-material like wood, due to temperature variations ; (3) dry quickly ; (4) produce a protective film (a hard, tough, durable and quite resistant to wear and tear) ; (5) produce glossy and shining film on drying ; (6) yield asthetical appealing film ; (7) yield elastic film, which does not crack or peel off on drying ; (8) yield film, whose colour does not fade or change on exposure to atmospheric weather ; (9) not shrink or crack after drying.

**Constituents of a varnish.** (1) **Resins** in use are : (a) *natural resins* (like shellac, kauri, rosin, copal, dammer, manila, etc.), and (b) *synthetic resins* (like phenol-aldehyde, alkyds, urea-formaldehyde, terpene polymers, etc.).

The resins, in general, are characterized by high resistance to weathering and chemical action, elasticity of film, good adhesion, high lustre, and in certain cases, high colour, stability to heat and light. Thus, resin in varnish provides an element of hardening, resistance to weathering, durability, resistance to chemical action and water-proofness.

(2) **Drying oils :** Principal oils used are linseed oil, tung oil, dehydrated castor oil, soyabean oil, oiticia oil, perilla oil, fish oil, etc. They dry by oxidation and polymerization.

(3) **Solvents or thinners**, usually, employed are turpentine, petroleum spirits, coal-tar naphtha, kerosene, xylol, tolyl, butyl and ethyl alcohols, amyl acetate, acetone, etc.

(4) **Driers** are added to enhance the drying rate of oil constituents. These include Pb, Co and Mn linoleates, napthenates, resinates, etc.

(5) **Antiskinning agent** like *tert*-amyl phenol, guiacol, etc.

**Uses of varnishes :** (1) For the protection of articles against corrosion ; (2) as a brightening coat to painted surface. Thus, surface is first coated with paint and over it is then applied a coat of varnish, which eliminates the effect of atmospheric oxygen, thereby preventing corrosion ; (3) for improving the appearance and intensifying the ornamental grains of wood surfaces.

## ✓16 ENAMELS

**Enamel** is a pigmented-varnish (i.e., an intimate dispersion of pigments in a varnish). They, on drying, give lustrous, hard and glossy finish. The properties of an enamel vary widely, depending



(2) **Vehicle** may be pure resin or oleoresinous. Natural resins (like rosin, etc.) (like alkyd resins) are used as pure resin vehicle. In *oleoresinous vehicles*, synthetic resins like phenol-aldehyde plus oil (like linseed, soyabean or fish oil) are used.

(3) **Driers** are used only in case of oleoresinous enamels. The commonly used driers are resinates and oleates of Co, Mn and Zn.

(4) **Thinner** commonly employed is turpentine or acetone.

## 17 LACQUERS

A **lacquer** is a colloidal dispersion of solution of a cellulose derivative, resin and plasticizer in solvent and diluents. Lacquer dries in air-principally by evaporation of solvents, yielding a transparent, hard and water-proof film.

**Constituents of lacquers :** 1. **Cellulose derivatives** (like cellulose nitrate, cellulose acetate ethyl cellulose, cellulose acetobutyrate etc.) provide : (i) *water-proofness*, (ii) *hardness*, and (iii) *durability* to the finish.

2. **Resins** used are phenol-aldehyde, alkyd, copal, dammer, eater gum, etc. Their function is to increase the solid contents so as to enhance : (i) *thickness of film*, (ii) *retention of original gloss*, (iii) *adhesion*, and (iv) *water resistance*.

3. **Plasticizers** like castor oil (raw or blown), blown soyabean oil, tricresyl phosphate, dibutyl phthalate, etc. are added to : (i) *reduce brittleness*, (ii) *improve adherence*, and (iii) *improve ductibility and flexibility of film*.

4. **Solvents** used are ethyl acetate, butyl acetate, ethyl lactate, methyl ethyl ketone, etc. Their function is to *dissolve the film-forming substance, viz., cellulose derivatives and resins*.

5. **Diluents** used are toluol, benzol, solvent naphtha, petroleum naphtha, etc. They are added to *reduce the viscosity (or consistency) as well as the cost*.

**Uses of lacquers :** (1) For interior decoration like paintings of wood work and furniture. (2) For giving a finishing coat to automobile bodies, due to their resistance to abrasion, cracking, chalking, etc. (3) In coating cotton fabrics, which are used in preparing artificial leathers, etc.

## 18 EMULSION PAINTS

**Emulsion paint** is essentially 'a dispersion' of rubber-like resin in water'. In addition, it contains film-forming vehicle (either drying oil or oleoresinous), pigment and extender. Besides these main constituents, emulsion paint may contain stabilizer, preservative, drier and antifoaming agent.

Emulsion paint can readily be *thinned or diluted* with water. When an emulsion paint is applied to a surface, water evaporates, emulsion breaks and oleoresinous particles coalesce to form a continuous, homogeneous and clear film.

Emulsion paint coatings are useful in *coating porous and / or wet surfaces*, because they have less penetrating power than solvent-containing coatings and they *wet readily moist surfaces*. Moreover, emulsion coats are *less odorous, non-inflammable, quick-drying and easier to apply* than ordinary paints or lacquers. *The resultant film resembles the conventional paint film, but is less water-resistant*, because of the presence of the residual emulsifying agent. Also such a paint can be *re-coated many times*.

**Constituents of emulsion paints :** (1) **Rubber-like resins** used are semi-solid polystyrene, polyvinyl acetate, butadiene copolymer, etc.

(2) **Oleoresinous materials :** Oils used are readily dispersible such as linseed oil; while *resins* used are alkyd resin, ester gum, polystyrene, etc.

(3) **Pigments** commonly used are mica, and water-dispersing like titanium dioxide.

(4) **Extenders** commonly used are mica, diatomaceous clay, silica and magnesium silicate.

(5) **Emulsifying agents** are used for dispersion of : (a) *rubber-like materials* are complex phosphates like tetra-sodium phosphate ; (b) *organic-type-pigments* are dioctyl sodium sulphosuccinate, sodium lauryl sulphate, etc.

(6) **Stabilizers** used are proteins like dextrin, starch, water-soluble gums, bentonite, casein, soya-protein, etc. A stabilizer imparts *chemical-resistance to the emulsion*. Moreover, the protein provides body, thereby improving brushing action.

(7) **Preservatives** are added to prevent the decomposition of any protein and to eliminate the growth of fungus. Important preservatives are mercuric chloride, thymol and chlorothymol.

(8) **Antifoaming agents** are added to check any excessive foam formation by the agitation of emulsion paints, during their manufacture. Important antifoaming agents are pine oil and kerosene.

(9) **Driers** are added to an emulsion paint, which contains *oxidisable oils*. They are Co, Mn, Zn resinate, phthalates, etc.

(10) **Volatile material** is mainly water. Aqueous ammonia is also used in some cases.

## 19 SPECIAL PAINTS

(1) **Luminescent paints** contain luminophor pigments, i.e., which fluoresce under the influence of UV light. Such pigments absorb UV (or other short-wavelength radiations) and emit radiations in the visible region of the spectrum. Luminophor pigments include ZnS or sulphides of Zn and Cd, titania with a small amounts of colour modifiers like Cu, Ag, Mn and B. called *activators*. It may be pointed out that these

produced by the break-down of the other components of paint. PVC, chlorinated rubber, alkyds (made from the tetrachlorophthalic anhydride), epoxides (made from the tetrabromo bisphenol-A), etc., break-down to give corresponding non-inflammable hydrogen halides; urea-formaldehyde resins yield  $\text{NH}_3$ ; carbonate pigments yield  $\text{CO}_2$ ; while water is obtained from water-based paints.

Paints containing magnesium ammonium phosphate, calcium ammonium phosphate, zinc ammonium pyrophosphate or zinc ammonium tungstate, etc., yield at elevated temperatures, a glass-like melt, which acts a barrier between air and the inflammable substrate, thereby hindering any combustion.

(4) **Cellulose paint** is made from nitro-cellulose and celluloid. It dries quickly and becomes hard, after addition of a thinner. Paint is non-inflammable, glossy, durable, but shrinks after drying. This paint is used in aeroplane and motor car industry, under the patented product DUCO.

(5) **Coal-tar paint** consists of a melt of coal-tar to which spirit thinner is mixed. It is always applied to the surface to be painted in hot condition. This paint, used for protecting iron and steel surfaces and materials, used under the ground.

(6) **Antifouling paints** are used in marine constructions. They specially contain antifouling agents like mercuric oxide, cuprous oxide, penta chloro phenol, phenyl mercury naphthenate, etc. which retard the fouling of ships, piers, etc. by marine worm, fungi, etc. and this helps in controlling their corrosion.

(7) **Cement paint** : The ingredients are : (i) white cement (about 70%) ; (ii) hydrated lime  $[\text{Ca}(\text{OH})_2]$  ; (iii) pigment (a colouring agent) ; (iv) very fine sand (an inert filler) ; (v) water-repellent compound. Usually, such paints of different colours are marketed in powder form (e.g., Snowcem, Smocem). The powder is mixed with a suitable quantity of water to get a thin slurry, which is then applied on plastered brick-work, concrete work, stone masonry, etc., both for interior and exterior surfaces. For application on corrugated iron surfaces, it is mixed with boiled-linseed oil.

**Note** : For good results, a 1.5 to 2% aqueous solution of sodium silicate and zinc sulphate is applied as primer

