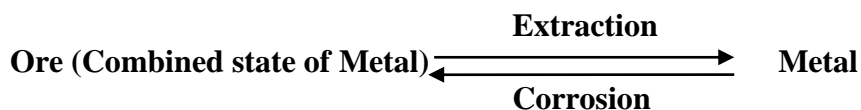


CORROSION CHEMISTRY

CORROSION- “Destruction, deterioration and loss of solid metallic material, starting at its surface by chemical or electrochemical attack.”

E.g.:- Rusting of iron, green deposits on copper surface etc.



THEORIES OF CORROSION (OR) MECHANISM OF CORROSION

1. Dry or Chemical corrosion.
2. Wet or Electrochemical corrosion.

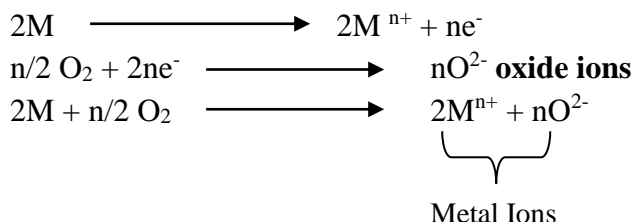
Dry or Chemical corrosion- It is due to direct chemical action of environment/ atmospheric gases[**Electronegative**] (O_2 , Cl_2 , H_2S , N_2) and anhydrous inorganic liquids on the metal surface[**Electropositive**].

Chemical corrosion is classified into two types-

a) **Oxidation corrosion**

It occurs due to direct action of oxygen at low or high temperatures on metals in the absence of moisture.

Mechanism



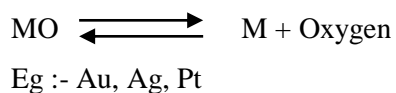
Oxidation occurs at the surface of metal and the resulting metal oxide scale, that acts as a barrier for further oxidation.

For further oxidation to continue a) the metal ion must diffuse outwards or b) oxide ion must diffuse inwards.

Former occurs more readily as because of the smaller size of the metal ion.

In oxidation corrosion, the nature of the oxide film plays an important role. It may be-

- a) **Stable** – A stable layer of metal oxide is formed which is impervious and this protects the metal from further corrosion. Eg :- Al, Sn.
- b) **Unstable**- The oxide layer decomposes back to metal and oxygen.



- c) Volatile- Oxide layer evaporates as soon as it is formed. Then by the metal surface is exposed for further attack. Eg :- MoO_3 .
- d) Porous- Oxide layer has porous or cracks, so oxygen has access to the underlying metal. Hence, corrosion continues.

Pilling – Bed worth rule-

It tells about the nature of the oxide layer- protective or non – protective.

"If the volume of the oxide film is greater than the volume of the meta surfacel, then the oxide layer is protective and non-porou"s.

On the other hand," if the volume of the metal oxide is less than the volume of the metal, then the layer is non-protective and porous".

Eg :- Alkali and alkaline earth metals form non-protective oxide film.

Al forms protective oxide film.

b) Corrosion by other gases (SO_2 , CO_2 , Cl_2 etc)

The extent of corrosion mainly depends on

- i) Affinity between metal and the gas.
- ii) Nature of the surface film.
- If the film protective or non- porous, further corrosion do not occur (attack of Cl_2 on Ag).
- If the film non- protective or porous, further corrosion occurs (attack of Cl_2 on Sn).
- c) **Liquid metal corrosion-** It occurs when a liquid metal at high temperature flowing on a solid metal. Here, the corrosion reaction involves dissolution of solid metal or external penetration of liquid metal into solid metal. Eg:- In nuclear power plants.

2. Wet or Electrochemical corrosion-

This Corrosion occurs when the environment favors the formation of anodic and cathodic areas on the metal,

- i) A metal is exposed to two different concentrations of environment.
- ii) Two different metals are in contact in a medium.

At anode:- Oxidation (Corrosion) takes place ie $\text{M} \longrightarrow \text{M}^{n+} + n\text{e}^-$

At cathode:- Reduction takes place, Where electrons are consumed.

Corrosion of an anode is based on how electrons are consumed at cathode
at cathode consumption of electron takes place either by

a) **Liberation / evolution of hydrogen** –occurs in acidic medium

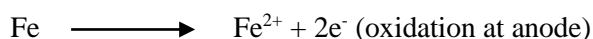
Eg: - $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$ (oxidation at anode)

$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ (reduction at cathode)

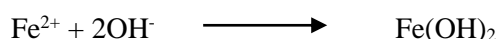
 $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2$

b) **Absorption of oxygen-** Occurs in neutral aqueous solution (NaCl solution) in the presence of atmospheric oxygen.

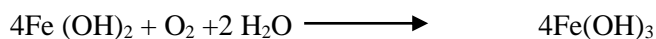
Eg:- Rusting of iron in presence of NaCl solution.



The Fe^{2+} combines with OH^- to form $\text{Fe}(\text{OH})_2$ precipitate.



In presence of sufficient amount of Oxygen,



In presence of limited amount of oxygen, black anhydrous magnetite is formed.

Factors affecting the corrosion

The rate of corrosion mainly depends on two factors.

- A. Nature of the metal
- B. Nature of corroding environment.

A. Nature of metal

1. Position in Galvanic series:-

When two different metals are in contact in presence of Medium, the more active metal (top in galvanic series) undergoes Corrosion. The rate of corrosion depends on difference in their positions

Galvanic series

2. Over voltage:-

When Zn is placed in 1N- H_2SO_4 , it undergoes corrosion by evolution of H_2 . The rate of corrosion is slow because of high overvoltage (0.77V) of Zn metal. If few drops of CuSO_4 is added, the corrosion of Zn is accelerated, because Cu deposited on Zn acts as minute cathode, where the evolution of H_2 is 0.33V.

Reduction in overvoltage accelerates the corrosion rate.

3. Relative areas of anodic and cathodic parts:-

Smaller the anodic area and larger the cathodic area severe will be the corrosion.

4. Purity of the metal:-

Impurities in a metal cause heterogeneity and forms minute electrochemical cells and anodic area gets corroded.

5. Physical state of metal:-

Rate of corrosion depends on grain size, orientation of crystals, stress etc. Smaller the grain size and area under stress, greater will be the corrosion.

6. Nature of surface film:-

The ratio of volume of metal oxide to metal is called "Specific volume ratio". Greater the specific volume ratio, lesser will be the oxidation corrosion.

Eg: Specific volume ratio of Ni, Cr, W are 1.6, 2.0, 3.6. Oxidation corrosion is least in W.

Mg

Zn

Al

Cd

Al alloys

Mild steel

Cast iron

Pb

Sn

Brass

Cu

Ni

Ag

Au

pt

7. *Passivity*:-

Metals like Ti, Al, Ca, and Mg are passive and they have high corrosion resistance. This is due to formation of protective oxide film having salt-heating nature.

B. Nature of the corroding environment-

- i. *Temperature*- The rate of corrosion increases with increase in temperature.
- ii. *Humidity of air*: - Rate of corrosion increases with increase in humidity and the relative humidity above which the rate corrosion increases sharply is called critical humidity.
- iii. *Presence of impurities in atmosphere*- Presences of gases like CO₂, H₂S and fumes of HCl increases acidity of liquid surrounding metals and increases corrosion.
- iv. *Presence of suspended particles*- Chemically active particles NaCl absorbs moisture and forms strong electrolyte enhances corrosion.
- v. *Influence of pH* :- Corrosion is more in acidic medium than neutral or alkaline medium.
Eg :- Zn corroded rapidly in weakly acidic solution and suffers minimum corrosion at pH =11.
- vi. *Nature of ions*- Presence of silicate leads to formation of insoluble corrosion products, which inhibits further corrosion.
- vii. *Conductance of the medium*- Dry sandy soils are less corrosive than clayey and mineralized soils.
- viii. *Formation of oxygen concentration cell* :- with increase in supply of oxygen to metal surface, the corrosion is promoted. Less oxygenated parts acts as anode and more oxygenated parts acts as cathode. This results in formation of “oxygen concentration cell”.

Types of Corrosion-

1. ***Galvanic corrosion or Bimetallic corrosion***- When two dissimilar metals are connected in an electrolyte, the metal higher in electrochemical series undergoes corrosion.

Eg:- Zn and Cu. Zn acts as anode and is protected & Cu acts as cathode.

At anode:- $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$

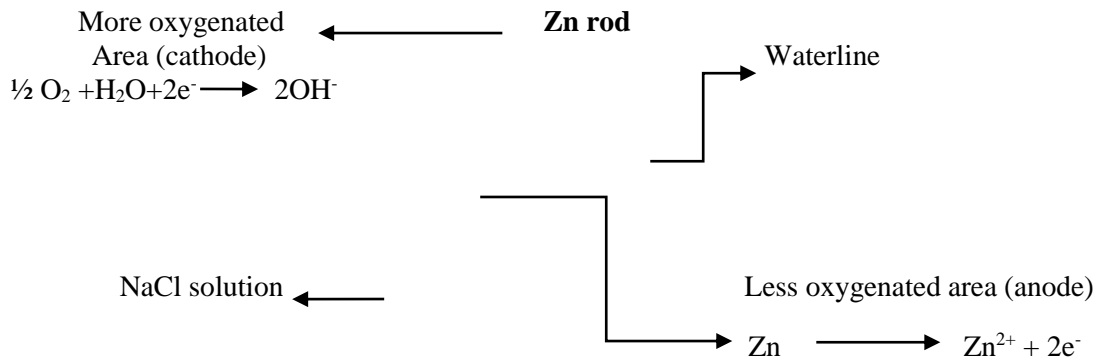
At cathode:- $2\text{H}^+ \longrightarrow \text{H}_2 \uparrow$

Eg:- Corrosion of

- 1) Steel screws in a brass marine hardware.
 - 2) Lead- Antimony solder around copper.
2. ***Concentration Cell corrosion***- It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration. This may be the result of local differences in metal ion concentrations.

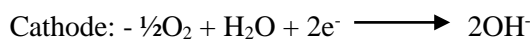
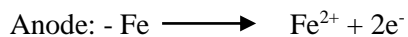
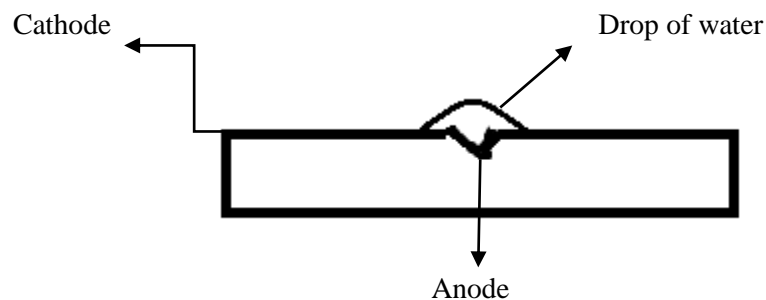
Differential aeration corrosion- The most common type of concentration cell corrosion occurs when different parts of the metal are exposed to different O₂ or air concentration. Less

oxygenated part acts as anode and undergoes corrosion, where as more oxygenated parts acts as cathode. A differential current flows from anode to cathode. E.g.: (1) - Zn rod in NaCl(aq)



When Zn is immersed partially in neutral NaCl solution, then the area below the waterline is less oxygenated acts as anode and undergoes corrosion. The area just above the waterline is more oxygenated acts as cathode.

Eg: (2) - Corrosion of iron under a drop of water (in salt solution)



3. **Pitting Corrosion**- It is a localized attack, resulting in the formation of cavities or holes around which the metal is unattacked. It is mainly due to breakdown of surface film at specific points which results in formation of smaller anodic and larger cathodic areas.

The breakdown of surface film is due to

- i. Surface roughness
 - ii. Scratches or cuts
 - iii. Local strain due to non uniform stress
 - iv. Alternating stresses
 - v. Sliding under load
 - vi. Chemical attack
- Metals such as stainless steel and aluminum shows pitting corrosion due to destruction of their passivity. E.g.:- Al in Chloride solution.
 - Presence of impurities like sand, dust on the surface of metals also leads to pitting. The area under the impurity acts as anode and surrounding areas acts as cathode.

4. **Stress corrosion**- It is highly localized attack on metal surface due to tensile stresses and corrosive environment. For stress corrosion to occur-
- Presence of tensile stress, and
 - Suitable corrosive environment is necessary.

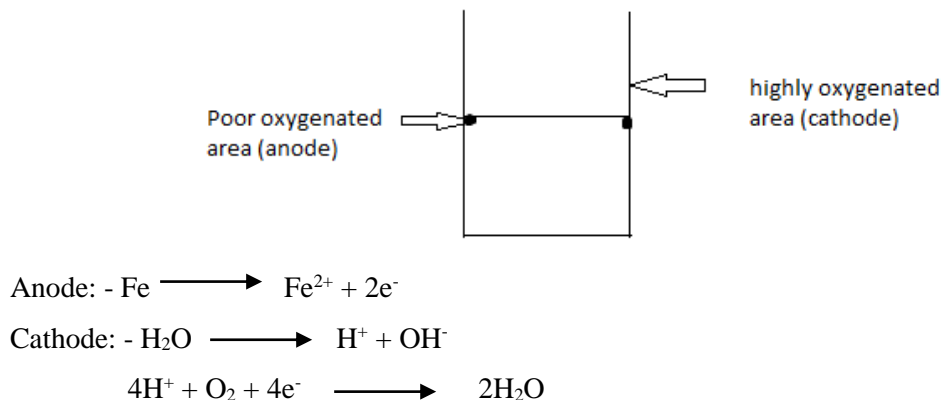
The corrosive agents are

- Caustic alkali and strong nitrate solution for mild steel.
- Ammonia for brass.
- Acid chloride solution for stainless steel.

This type of corrosion is observed in fabricated alloys, like brass, which experiences high stress under working conditions like rolling, drawing, insufficient annealing. Presence of stress produces strain, which results in localized zones of higher electrode potential. These are chemically active and are attacked.

E.g:- Caustic embrittlement- a type of stress corrosion occurs in mild steel exposed to alkaline solutions at high temperature in boilers.

5. **Waterline Corrosion**- When water is stored in a steel tank, maximum amount of corrosion occur along a line part below the water level.



6. **Intergranular corrosion**- This type of corrosion occurs along grain boundaries where the material is sensitive to corrosive attack and the corrosive liquid has a special character of attacking only at grain boundaries.

This type of corrosion is due to certain materials at grain boundaries, which are more anodic than that of grain centre.

Precipitation of certain compounds at grain boundaries results in solid metal solutions just adjacent to grain boundaries depleted in one constituent. This depleted region is anodic with respect to grain centre and precipitation compounds. So, it will be attacked preferentially.

E.g:- Welding of stainless steel (alloy of Fe, C, Cr).

Corrosion control or Protection against corrosion-

The most commonly used methods to control corrosion are

- Selection and design of materials.

- Cathodic and anodic protection.
- Use of corrosion inhibitors.
- Protective coatings.

a) **Selection and design of material-**

- The design of material should be such that of corrosion occurs it should be uniform and not localized.
- Avoid contact between dissimilar materials in presence of a conducting medium.
- When two different metals are in contact, then the anodic area should be large.
- Whenever contact between two dissimilar metals is unavoidable, an insulating material should be placed in between them.
- The anodic metal should not be painted or coated.
- The equipment should be supported on legs to allow free circulation of air.

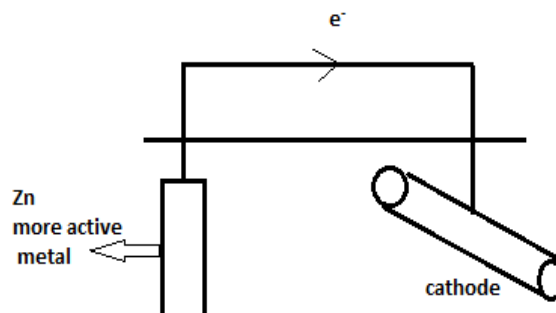
b) **Cathodic protection-**

Principle- The metal to be protected is forced to behave like cathode, thereby corrosion does not occur.

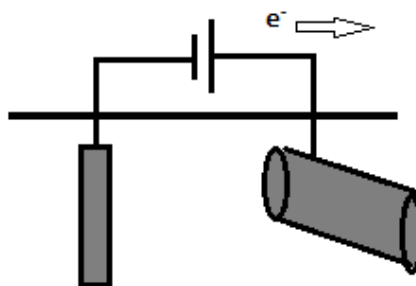
There are two types of cathodic protection

- i) ***Sacrificial anodic protection-*** In this method, the metallic structure (to be protected) is connected to more anodic material. So, that the corrosion is concentrated at more active metal. The more active metal sacrifices itself by corrosion and protects the structure (cathode). The sacrificial anode are Zn, Mg, Al.

This method is mainly used for protection of underground pipeline, cables, and marine structures.



- ii) ***Impressed current cathodic protection-*** In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. The impressed current is derived from a direct current source like a battery. Sufficient D.C current is applied to an insoluble anode, buried in the soil and connected to the metallic structure to be protected. This type of cathodic protection is applied to open water-box coolers, water-tanks, buried oil or water pipes etc.



c) **Use of corrosion inhibitors**- A corrosion inhibitor is a substance which when added in small quantities to the aqueous corrosive environment and effectively decreases the corrosion of the metal. Inhibitors are-

- i) **Anodic inhibitors**- they control the corrosion reaction occurring at the anode, by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface, forming a protective film or barrier, thereby reducing the corrosion rate. E.g.:- Transition metal ions with chromates, phosphates, tungstates etc.
- ii) **Cathodic inhibitors**- In acidic medium, the corrosion rate can be reduced either by slowing down the diffusion of hydrated of hydrogen ions to cathode or by increasing the overvoltage of hydrogen evolution. In natural solutions, corrosion can be controlled by either by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathode areas.

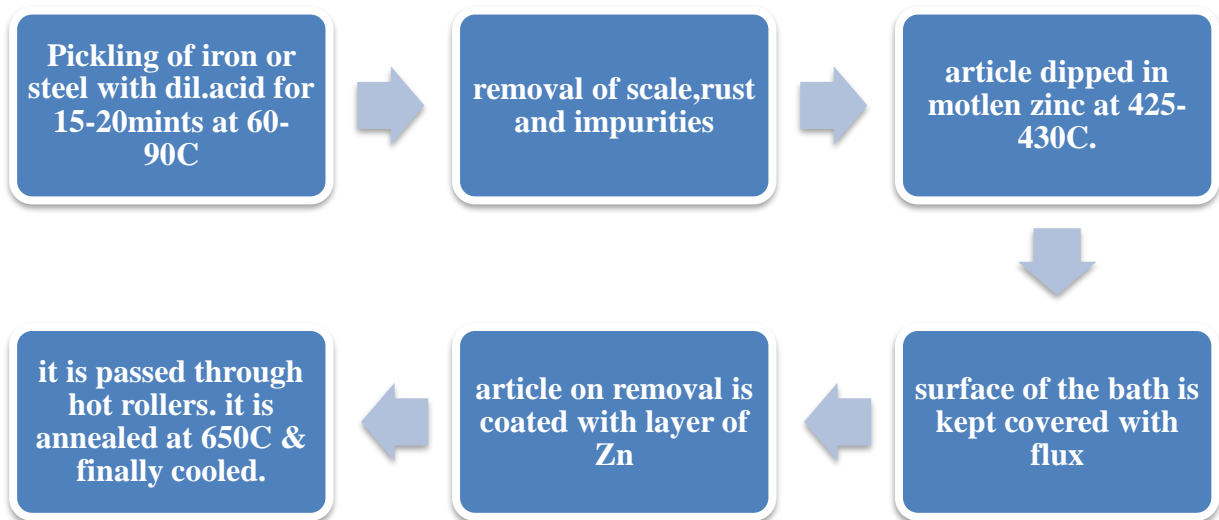
d) **Protective coatings**:- Limitations of this method are i) the coatings should be chemically inert (ii) coatings must prevent the penetration of the environment to the metal.

- **Anodic coatings**- They are produced from coating-metals which are anodic to the base metal. E.g.:- coating of Zn, Al, Cd on steel are anodic as their electrode potentials are lower than that of the base metal, iron. If any pores, breaks occur, a galvanic cell is formed between the coating-metal and the exposed part of the base metal. Galvanization is based on this principle.
- **Cathodic coatings**: - They are obtained by coating a more noble metal, having more electrode potential than the base metal. They have higher corrosion resistance than the base metal. Cathodic coatings provide effective protection to the base metal only when they are completely continuous and free from porous, breaks.

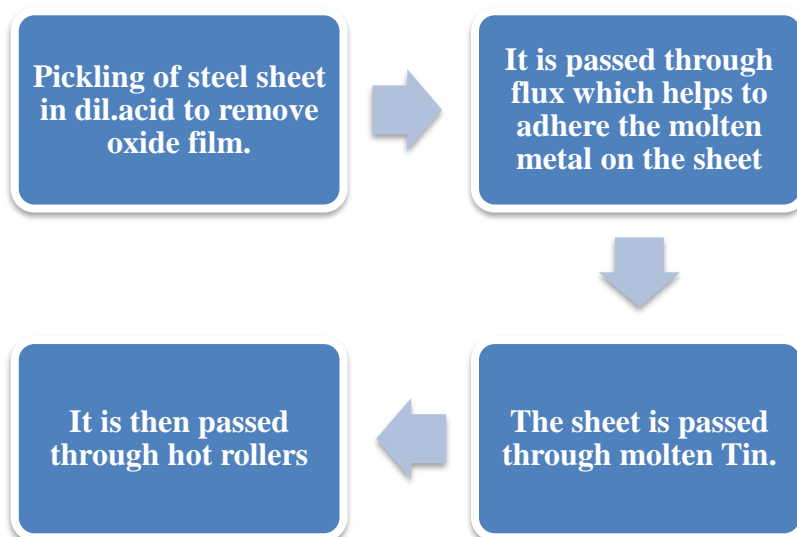
Methods of application of metal coatings-

1. **Hot dipping**- The process involves immersing the base metal in a bath of the molten coating-metal covered by flux layer. Mostly used hot dipping methods are-

- a) **Galvanization**- It is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. Series of steps involved in the process is described below.



- b) **Tinning**- It is the process of coating tin over the iron or steel articles to prevent them from rusting. Series of steps involved in the process is described below.



- 2) ***Metal cladding***- a dense homogenous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides. E.g. a plate of duraluminium is sandwiched two layers of pure aluminum.
- 3) ***Electroplating***- coating metal is deposited on the base metal by passing a direct current through an electrolyte solution, containing the soluble salt of the coating metal.
E.g- Copper plating.

- 4) **Immersion Plating-** Immersion of the base metal in the electrolytic solution of cathodic coating metal. The deposition occurs by simple displacement. The ions of the cathodic metal are displaced from the salt solution by ions of the base metal.
E.g: Kanigen process of Nickel plating involves immersion of base metal in a bath of Nickel sulphate and sodium hypophosphate.
- 5) **Metal spraying-** Coating metal in the molten form is sprayed on the rough surface of the base metal.
- 6) **Cementation or diffusion coating-** obtained by heating the base metal in a revolving drum containing a powder of the coating metal. Diffusion of coating metal into base metal takes place resulting in a layer of alloy of varying composition.
- Sheradizing- cementation using Zinc powder
 - Colorizing- cementation using Aluminum powder and Aluminum Oxide.
 - Chromising- cementation using Chromium powder and alumina.
- 7) **Chemical conversation coatings-** they are inorganic-surface barriers, produced by chemical or electrochemical reactions, brought at the surface of the base metal. These coatings are applied as follows-
- Phosphate coatings-* produced by chemical reaction with aqueous solution of phosphoric acid and phosphates of Fe, Mn, Zn etc.
 - Chromate coatings-* produced by immersion of the article in a bath of acidified potassium chromate, followed by immersion in a bath of neutral chromate solution.
 - Chemical oxide coatings-* produced by treating the base metal with alkaline oxidizing solution or gas.
 - Anodized coatings:-* produced by anodic oxidation process, in which the base metal is made as anode. They are produced on non-ferrous metals like Al, Zn etc.

Organic Coatings :- They are inert organic-barriers (like paints, varnishes, lacquers and enamels) applied on metallic surfaces for corrosion protection.

Paints:- It is a mechanical dispersion mixture of one or more pigments in a vehicle. Vehicle is a liquid, consisting of non-volatile, film-forming material, a drying oil and a highly volatile solvent, thinner.

Mechanism- when paint is applied, the thinner evaporates, while the drying oil slowly oxidizes forming a dry pigmented film.

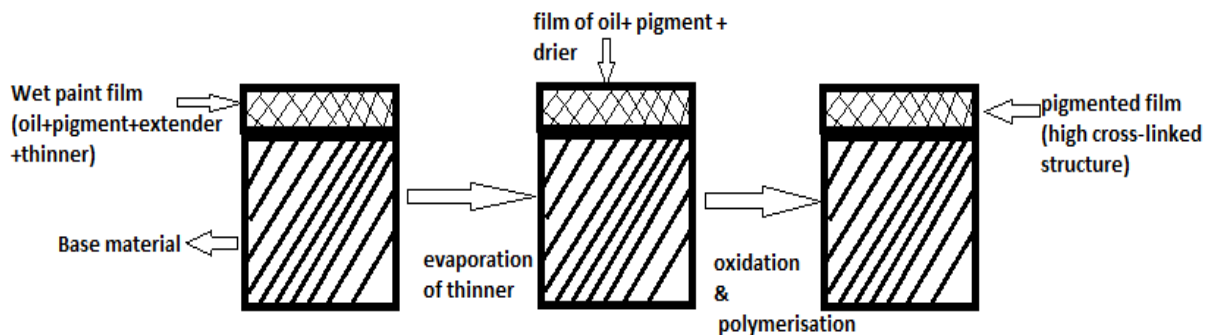
Constituents of paints-

1. Pigment-

- Provides capacity, strength & color.
- Gives protection to the paint film by reflection harmful UV light.
- Provides resistance to paint film against abrasion/water.
- Pigments used whites (Titanium oxide, zinc oxide), black- carbon black, and green- chromium oxide.

2. *Vehicle or drying oil-*

- Film – forming constituent.
- Glycerol esters of high molecular-weight fatty acids present in animal and vegetable oils. Mostly used drying oils are linseed oil, soyabean oil.



3. *Thinners-*

- Reduces viscosity.
- Dissolves vehicle, additives of vehicle.
- Increases the penetration power of vehicle.
- Increases the elasticity of paint film.
- Common thinners are turpentine, mineral spirits, benzene, dipentene etc.

4. *Driers-*

- Oxygen- carrier catalysts.
- Accelerates the drying of the oil-film through oxidation, polymerization and condensation.
- Improves the drying quality of oil-film.
- Common driers are tungstates, resonates etc.

5. *Extenders-*

- Low refractive indices materials.
- Increases durability of paint.
- E.g:- barites, talc, gypsum, china-clay.

6. *Plasticizers-*

- Provides elasticity.
- Minimizes cracking.
- Common plasticizers are triphenyl phosphate, tributyl phthalate etc.

7. *Antiskinning agent-*

- Prevents gelling and skinning. Polyhydroxy phenols are used.

Varnishes-It is a homogenous colloidal dispersion solution of natural or synthetic resin in oil or thinner or both. It acts as a protective layer by evaporation, oxidation and polymerisation of the constituents.

Types of varnishes-

- a) Oil varnish- homogenous solution of one or more natural or synthetic resins in a drying oil and volatile solvent.
- b) Spirit varnish- contains resins dissolved in a volatile solvent.

Constituents of varnish-

1. **Resin-**
 - Natural resins (shellac, dammer etc)
 - Synthetic resins (phenol-aldehyde, urea-formaldehyde etc).
2. **Drying oils-**
 - Oils like linseed oil, soyabean oils are used.
 - They dry by oxidation and polymerisation.
3. **Solvents or thinners-**
 - Turpentine, petroleum spirits etc are used.
4. **Driers-**
 - Enhance the drying rate of oil constituents.
 - Pb, Co linoleates etc.
5. **Antiskinning agents-**
 - Tert-amyl alcohol, guaiacol etc are used.

Lacquers- It is a colloidal solution of a cellulose derivative, resin and plasticizer in solvent and diluents.

Constituents of lacquers-

1. **Cellulose derivatives-**
 - Water-proofness, hardness and durability.
 - Cellulose nitrate, cellulose acetate etc are used.
2. **Resins-**
 - Gives thickness and adhesion to the film.
 - Phenol-aldehyde, eate gum etc.
3. **Plasticizers-**
 - Reduces brittleness and improves adherence.
 - Castor oil, soyabean oil etc.
4. **Solvents-**
 - Dissolves film-forming substances like cellulose derivatives, resins.
5. **Diluents-**
 - Reduces viscosity.
 - Benzol, petroleum naphtha etc are used.