

UNIT-4

CORROSION ENGINEERING

Defination:

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium. The process of decay metal by environmental attack is known as corrosion. Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc.

E.g.

Iron undergoes corrosion to form reddish brown colour rust [$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$].

Copper undergoes corrosion to form a green film of basic carbonate [$\text{CuCO}_3 + \text{Cu}(\text{OH})_2$]

Causes of corrosion:

1. The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
3. Hence the isolated pure metals are regarded as excited states than their corresponding ores.

So metals have natural tendency to go back to their combined state (minerals/ores).

When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts and forms more thermodynamically stabled compounds.

Effects of corrosion:

1. Wastage of metal in the form of its compounds.
2. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
3. Life span and efficiency of metallic parts of machinery and fabrications is reduced.

Theories of corrosion:

Basing on the corroding environment and the mechanism of corrosion, corrosion is classified into 2 types.

- 1) Dry corrosion or Chemical corrosion

2) Wet corrosion or electrochemical corrosion

Dry corrosion or Chemical corrosion

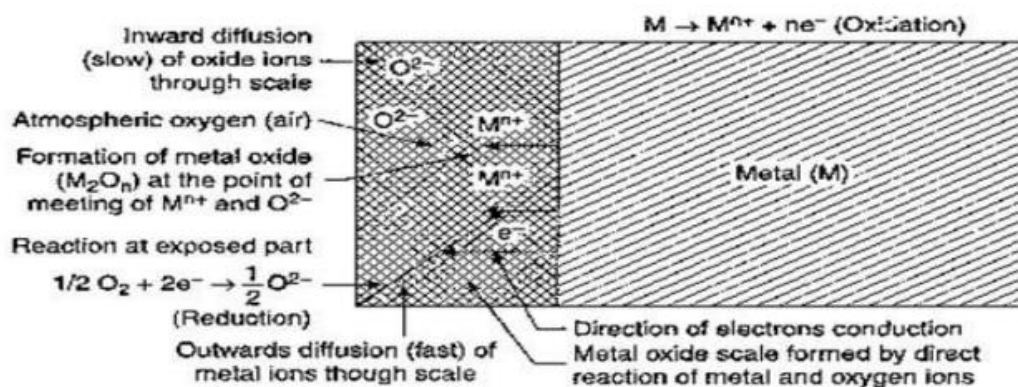
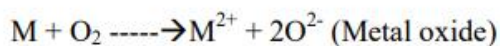
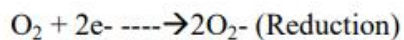
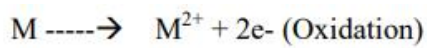
This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O₂, halogens, H₂S, SO₂, N₂ or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

- 1) Oxidation corrosion
- 2) Corrosion due to other gases
- 3) Liquid metal corrosion

1) Oxidation corrosion

This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, and Pt).



Mechanism: Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

(a) Stable, Protective and non-porous oxide film: If the metal oxide is stable, it behaves as a protective layer which prevents further Corrosion. E.g., the oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

(b) Unstable oxide film: If the metal oxide unstable, the oxide layer formed decomposes back into metal and oxygen. Oxidation corrosion is not possible. E.g. Ag, Au and Pt do not undergo oxidation corrosion.

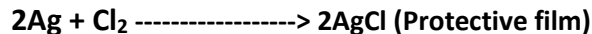
(c) Volatile oxide film: If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO_3).

(d) Porous / Non-protective oxide film: If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed. E.g. Alkali and alkaline earth metals (Li, Na, K, Mg etc.)

(2) Corrosion due to other gases:

This type of corrosion is due to gases like SO_2 , CO_2 , Cl_2 , H_2S , F_2 etc. In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent; non-porous does not allow the penetration of corrosive gases.



(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms Pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

(3) Liquid metal corrosion:

This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors

Wet corrosion or electrochemical corrosion

- This type of Corrosion occurs where a conducting liquid is in contact with the metal. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- At anodic area, oxidation reaction occurs there by destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.



The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

Evolution of hydrogen: This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with Liberation of electrons.

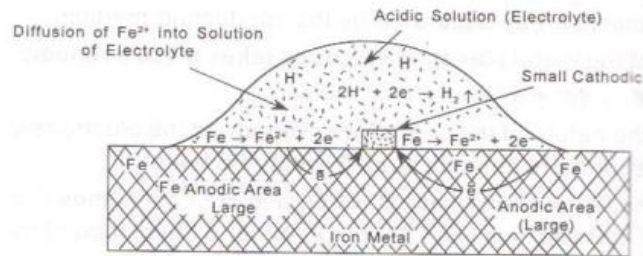
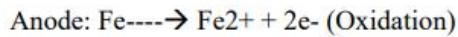
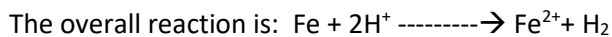
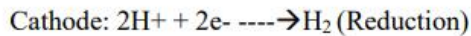


Fig.1.18 Hydrogen evolution corrosion



The electrons released flow through the metal from anode to cathode, whereas H^{+} ions of acidic solution are eliminated as hydrogen gas.



This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas. The anodes are large areas, whereas cathodes are small areas.

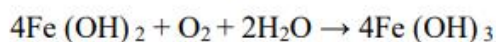
Absorption of oxygen: For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large Cathodes. The released electrons flow from anode to cathode through iron metal.

At anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation)

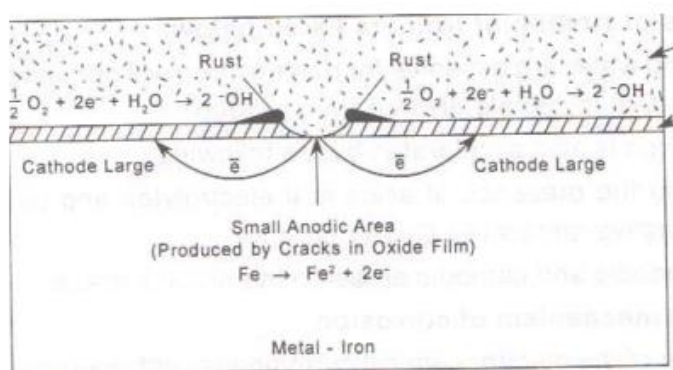
At cathode: $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (Reduction)

Overall reaction: $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$

If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



The product called yellow rust corresponds to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.



Factors effecting corrosion

The rate and extent of corrosion depends upon various factors due to nature of metal and nature of corroding environment.

Factors due to nature of metal

1. **Purity of the metal:** Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.
2. **Electrode potentials:** metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (eg. Zn, Mg, Al etc.).
3. **Position of metal in galvanic series:** Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.
4. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected. When two metals are in electrical contact in presence of an electrolyte, then the metal
 - which is more active undergoes corrosion. The rate of corrosion depends on the difference in their position in Galvanic series.
 - Greater the difference more will be the extent of corrosion at anode.

Eg. The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn. on this account, the use of dissimilar metals should be avoided wherever possible (Eg. Bolt & nuts, screw & washer).

- 5. Nature of surface film:** If the corrosion product formed is more stable, insoluble and nonporous, it acts as protective layer and prevents further corrosion (Eg. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

Factors due to nature corrosive environment

- 1. Temperature:** the rate of corrosion reactions increases with increase in temperature.
- 2. Humidity in air:** the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.
- 3. Presence of impurities:** Atmosphere is contaminated with gases like CO₂, SO₂, H₂S; fumes of H₂SO₄, HCl etc. and other suspended particles in the vicinity of industrial areas. They are Responsible for electrical conductivity, thereby increasing corrosion.
- 4. P H value:** pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.
- 5. Amount of oxygen in atmosphere:** As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

CORROSION CONTROL METHOD:

Corrosion is an inevitable (cannot be avoided) process. But by adopting certain methods it can be minimized and prevented.

- Proper selection and designing of metals
- Use of corrosion inhibitors
- Cathodic protection method
- Application of metallic coatings.
- **1.Proper selection and designing of metals**
- Proper selection and designing of metals reduces rate of corrosion. Designing and selection should be as follows.
- Avoid the contact of two dissimilar metals in corrosive environment, when they are in contact see that it posses higher anodic area and smaller cathodic area.

Two dissimilar metals form galvanic series must have very close positions, so that minimum corrosion occurs.

- Avoid the contact of two metals by insulating material.
- Avoid sharp ends and edges.
- Avoid capillarity at the bolt region.
- Avoid painting at anodic areas.

USE OF CORROSION INHIBITORS: Substances which when added in small quantities inhibit the process of corrosion are known as corrosion inhibitors.

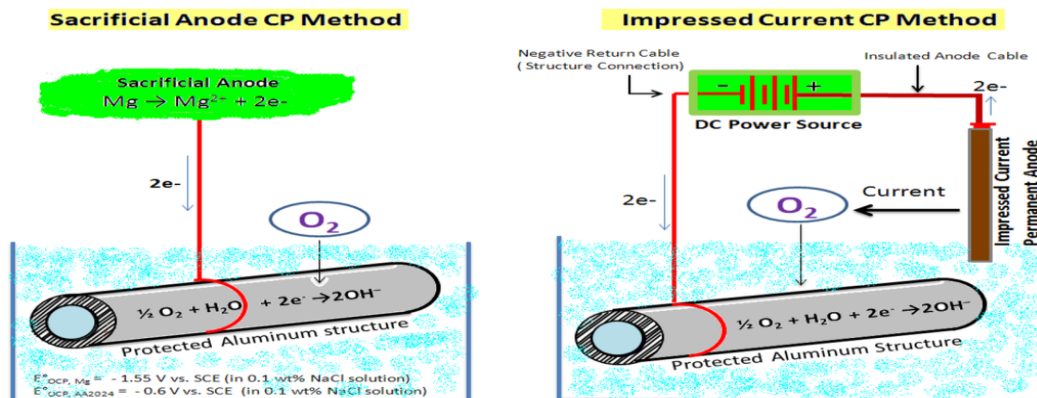
- Anodic inhibitors: These stop corrosion at anode by forming a compound with newly formed metal ion
- $M \rightarrow M^{n+}$
- It gets absorbed on the surface forming a protective film, reducing the corrosion.
Eg: Tungstates, phosphates & chromates
- Use of cathodic inhibitors: These stop corrosion at cathode in acidic medium by absorbing the H^+ ion formed at cathode. H^+ ion stops the formation of H_2 gas. Eg: Amines, mercaptans and heterocyclic nitrogen compounds

CATHODIC PROTECTION METHOD:

In this method, the metal to be protected is forced to act as cathode thus avoiding its corrosion. This can be achieved by

(a) Sacrificial anode protection

(b) Impressed current cathodic protection



Cathodic Protection (CP) Methods

- (a)**Sacrificial anodic protection:** The base metal (structure) is connected to more anodic metal through a wire. The anodic metal undergoes corrosion slowly and base metal is protected. The commonly used anodic metals are Mg and Zn. It is used to protect marine structures and buried pipelines
- **Impressed current corrosion control:** In this method an impressed current little more than corrosion current is applied in opposite direction to nullify the corrosion current producing a reverse cell reaction. The impressed current is taken from a battery and the anode is insoluble metal like graphite, scrap iron, platinum. The anode is kept in a “black fill” composed of coke/clay and gypsum.

Disadvantages:

Due to stray current produced during cathodic protection, adjacent structures will be effected.

- Capital investment and maintenance cost are high.
- Special care should be taken, over care should not be taken.,

Note: Apart from these cathodic protection is an excellent protection method.

Surface coatings:

- **Methods of application on metals (or):APPLICATION OF METALIC COATINGS:**
- Application of continuous, non-porous and chemically inert material on the surface of one metal by another metal is called as metallic coatings.
- These coatings act as a physical barrier and protects the base metal from corrosion.
- The coating metal may either act as Anodic or Cathodic to the base metal
- The metallic coatings often used are Zn, Sn, Ni, Cu, Cr,Al, Pb.

The following are various methods of metallic coatings

- Hot dipping
- Electro plating
- Electro cladding
- Electroless plating
- Metalcladding

Metallic coatings: Coating a metal on another metal in order to protect the base metal from corrosion. it is broadly of two categories.

(a)Anodic coating

(b) cathodic coating

(a)**Anodic coating:** In this method more anodic metals are coated on to the base metal. Eg: Zn, Al, Cd on iron. If any pores, breaks or cracks occurs exposing the base metal, the coating metal acts as anode and the base metal acts a cathode. Hence no corrosion occurs to the base. Until the coating metal corrodes.

(b) **Cathodic coatings:** This is obtained by coating a noble metal (having higher reduction potential) on to the base metal. Eg: Tin on the surface of iron. It gives complete protection only when the coating metal is continuous, non-porous, free from breaks etc.

When there are cracks in the protective coating, intense localized corrosion takes place due to smaller anodic area and larger cathodic area.

Methods of application of metallic coatings:

Hot dipping methods: The base metal is dipped in a molten bath of coating metal (usually low melting metals such as Zn, Sn, Pb, Al) covered with a molten flux. Flux is useful in preventing oxidation of coating metal; cleans the metal surface (for better adhesion) most widely used hot dipping methods are

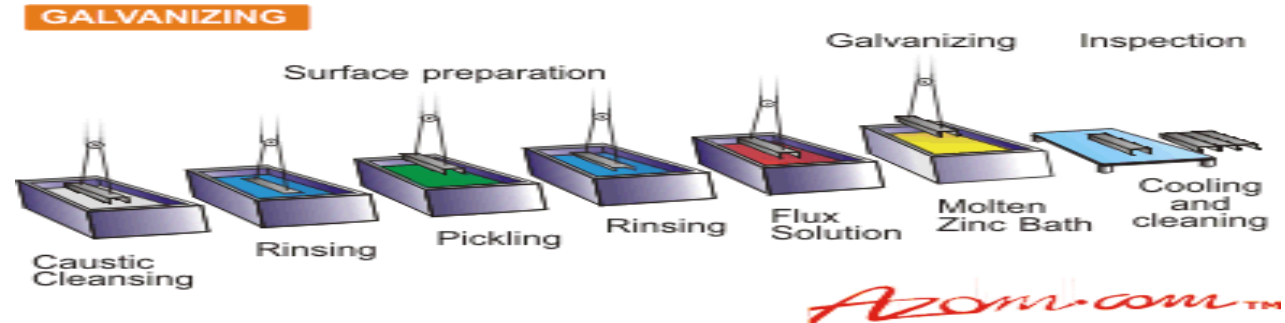
- Galvanizing (b) Tinning

Galvanizing: -> Coating of Zinc on Iron

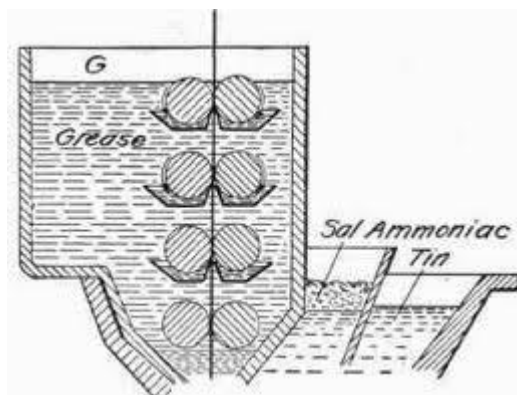
Base metal (Fe) is pickled with ion H_2SO_4 for 20mins at a temperature of 60-90°C and then sent to molten zinc bath maintained at 425-450°C. The surface of the bath is kept covered with NH_4Cl flux to prevent oxide formation. The excess Zinc on the sheet is removed and subjected to annealing at 650°C and cooled slowly.

The alloy of Zn and Fe will be formed at the function.

Application: Iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets and tubes.



Tinning: -> Coating of tin over Iron



Surface of the base metal is pickled with H_2SO_4 and passed through a bath of zinc chloride flux. The flux help the molten metal to adhere to base metal surface. The sheet is then passed through Tin and then through palm oil. It is then sent through rollers to produce uniform concentration and thickness. An alloy of Tin and Iron is formed at the function

Application:

- Tin metal posses good resistance against atmospheric conditions
- Used in food storage, ghee, oils etc,.
- Tinned Cu sheets are used in cooking utensils and refrigeration equipment.

DIFFERENCES BETWEEN GALVANIZING AND TINNING:

GALVANIZING	TINNING
<ul style="list-style-type: none"> • Coating on iron with zinc. • It protects the metal sacrificially. • Protection continues even if coating is broken. • Food materials cannot be stored in Zn coated containers as its compounds are toxic 	<ul style="list-style-type: none"> • Coating of iron with tin.] • Protection is due to the noble character of tin. • Protection is provide3d only when coating is perfect. • Tin coating is not toxic hence food materials can be stored.

ELECTROPLATING METHOD:

This method often uses coating copper, Nickel, Zinc, Lead, Tin, Gold and Silver.

Process: In this method an electrolytic cell is set up as follows for coating base metal with protective metal.

Electrolyte: A salt solution of protective metal

Anode: Protective metal in its pure form

Cathode: The metal to be coated/protected(base metal)

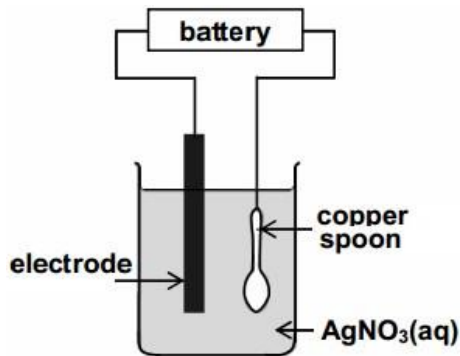
Reactions: At anode: $2 \text{M} \longrightarrow 2 \text{M}^{+n} + n\text{e}^-$

At cathode: The dissolved protective metals gets deposited on the cathode/base metal/parent metal forming a protective layer. $2 \text{M}^{+n} + n\text{e}^- \longrightarrow 2 \text{M}$

Factors effecting electroplating:

- Cleaning of article is essential for strong adherent electroplating.
- Concentration should be low for uniform, coherent metal deposition
- Additives such as glue, boric acid etc should be added for strong adhesion.
- Electrolyte should not under go any chemical reactions

- PH of the electrolyte should be properly maintained
- If anode is made of graphite, the electrolytic salt is added continuously to maintain proper coating metal ion concentration in the electrolyte bath.



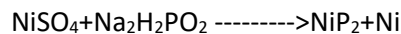
ELECTRO LESS PLATING:

- This is also known as immersion plating or displacement plating. It is done in the presence of an reducing agent instead of using electric power for the deposition of protecting metal.
- The base metal is dipped in a solution of noble metal salt. Then the noble metal ions are displaced from salt solution and gets deposited on base metal. Thus form a uniform and the thin layer on the base metal as a protective layer. It is catalytically carried out in the presence of a reducing agent.

Eg: Nickel plating

Salt solution: A mixture of Nickel sulphate (NiSO_4) solution and sodium hypophosphite ($\text{Na}_2\text{H}_2\text{PO}_2$) AS A REDUCING AGENT AT Ph 4.5-5.0 and 100C

During the electroless plating



A mixture of Ni and Ni P₂ forms a thin and uniform layer on the base metal resulting as nickel electroless coating providing corrosion resistance to the base metal.

APPLICATIONS:

- Electroless nickel is used in Aero space, plastics, Automotives etc.
- Electro less copper is used on non conductive substrates in printed circuit board manufacturing.

Electroless Ni plating are used in electronic application providing non magnetic underlay in magnetic components.

Metal cladding: In this method metal to be protected is sandwiched between the two layers of the protecting metal. These layers of the protecting metal are bonded firmly to the base metal by pressing the whole combination between rollers under the action of heat and pressure. The metals generally used as Ni, Cu, Pb, Ag.

Surface coatings:

The application of surface coating is the common method to protect the surface of the metal from the corroding environment. These surface coatings exhibit chemical inertness to corrosive environment, adhesive properties and impermeable.

a. Organic surface coatings

- Organic surface coatings are applied over the metallic surfaces to prevent from the corrosion.
- Properties of Organic surface coatings.
- Chemical inertness to the corrosive environment
- Good surface adhesion
- Impermeability to water, gases and salts Eg. Paints
- Paint is a mechanical dispersion mixture of several constituents in a vehicle oil or drying oil.
- The following are the constituents of paints and their functions.

Constituent Functions Examples

1. Pigment

- It is a major constituent of the paint.
- Provides desired colour to the paint
- It protects the paint by reflecting harmful U.V radiation.
- Gives strength and increases weather resistance of the film.
- White- white lead, ZnO
- Red- Red lead,
- Ferric oxide

2. Vehicle oil/ Drying oil

- It forms the film forming constituent of the paint.
- It acts as medium for the dispersion of various constituents.
- It gives durability, adhesion and water proofness to the paint.
- Sunflower oil, Mustard oil, Soya bean oil.

3. Thinners

- Reduces the viscosity and increases the elasticity of the Paint film.
 - Turpentine, Kerosene, Naphtha.
- ### 4. Driers
- Driers are oxygen carrying catalysts.
 - They accelerate the drying of the paint film through oxidation, polymerization and condensation.
- Tin states and naphthalates of Pb, Zn and Co.
- ### 5. Extenders/ Fillers

- Low refractive indices materials.
- They reduce the cost and cracking nature of the paint film.
- BaSO₄, gypsum,

6. Plasticizers

- They provide elasticity to the film and minimize cracking.
- Tributylphosphate,
- triphenylphosphate

7. Anti skinning agents

- They prevent the gelling nature of the paint film.
- Polyhydroxy phenols

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