

Glass electrode:

When two solutions of different P^H values are separated by a thin glass membrane. There develops a difference of potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in P^H value. The glass membrane functions as an ion-exchange resin.

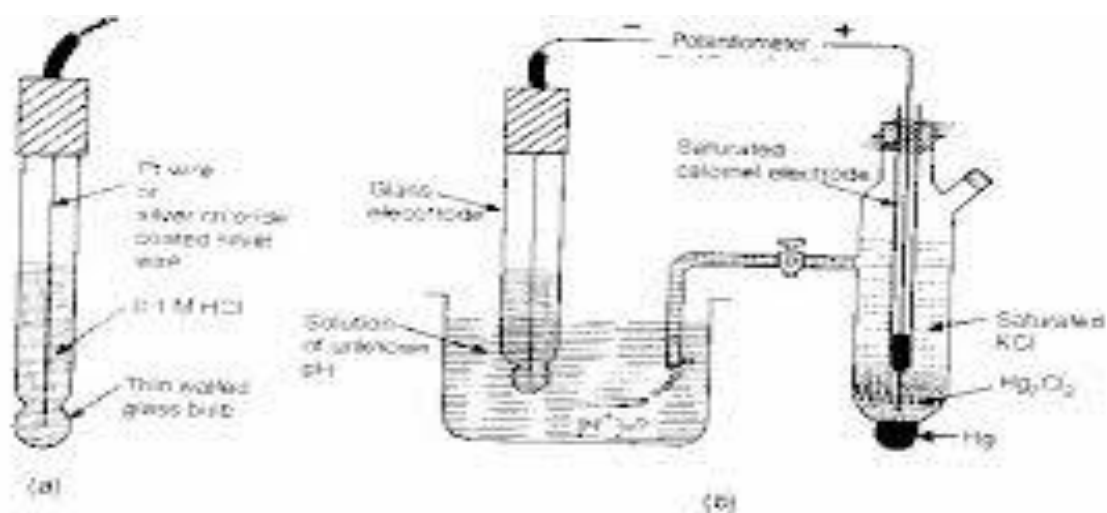
$$E_G = E_G^0 + 0.0592V P^H$$

Construction:

A glass electrode of thin-walled glass bulb containing AgCl coated Ag electrode or simply a Pt electrode in 0.1 M HCl. The glass electrode may be shown schematically as:

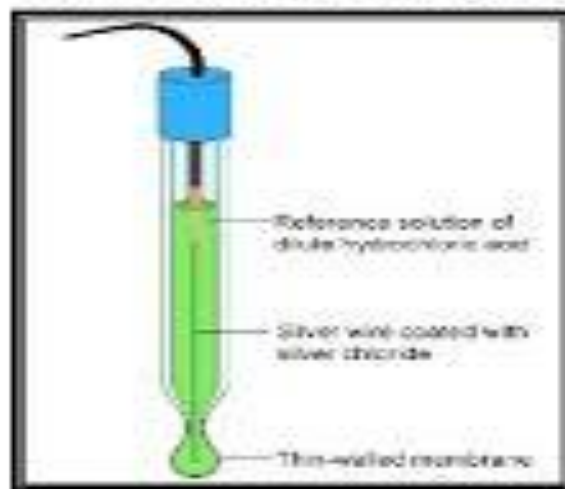


Glass electrode is used as the internal reference electrode for determining the P^H of solutions, especially coloured solutions containing oxidizing or reducing agents. Usually, calomel electrode is used as the second electrode. In order to determine the P^H of a solution, the glass electrode is placed in the solution under-test and this half-cell is coupled with saturated calomel electrode. The e.m.f. of the cell is measured. Since the resistance is very high. So special electron tube voltmeters are used to measure the e.m.f. of the above cell. The e.m.f of the complete cell is given by:



(a) Glass electrode ; (b) determination of pH by using glass electrode.

Glass electrode diagram



$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= 0.2422\text{V} - (E^0_G + 0.0592\text{V } P^H)$$

$$P^H = \frac{0.24422\text{V} - E_{\text{cell}} - E^0_G}{0.0592\text{V}}$$

The E^0_G value of glass electrode can be determined by using a solution of known Ph.

Advantages: It is simple and can easily be used.

1. Equilibrium is rapidly achieved.
2. The results are accurate
3. It is easily not poisoned

CORROSION CONTROL (PROTECTION AGAINST CORROSION)

As the corrosion process is very harmful and losses incurred are tremendous, it becomes necessary to minimize or control corrosion of metals. Corrosion can be stopped completely only under ideal conditions. But the attainment of ideal conditions is not possible. However, it is possible only to

minimize corrosion considerably. Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so different, diverse methods are used to control corrosion. As the corrosion is a reaction between the metal or alloy and the environment, any method of corrosion control must be aimed at either modifying the metal or the environment.

a. Choice of metals and alloys:

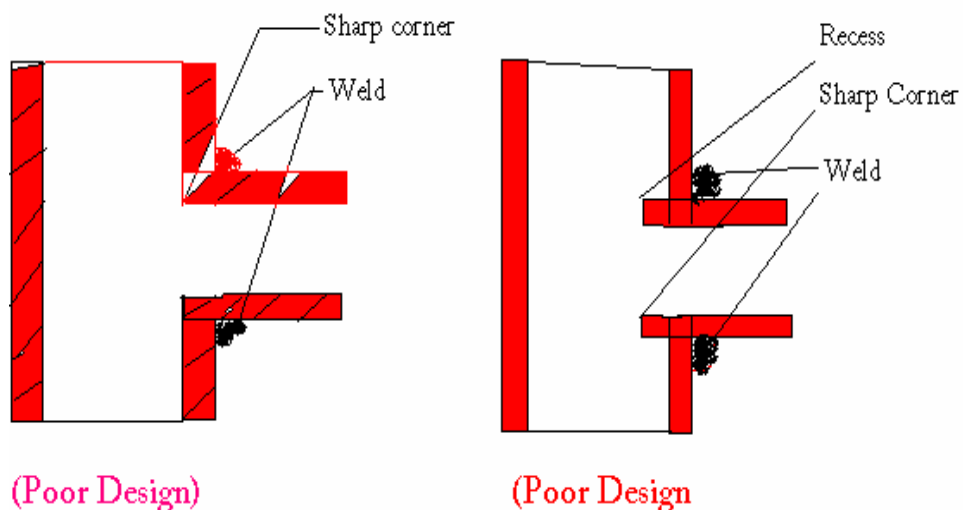
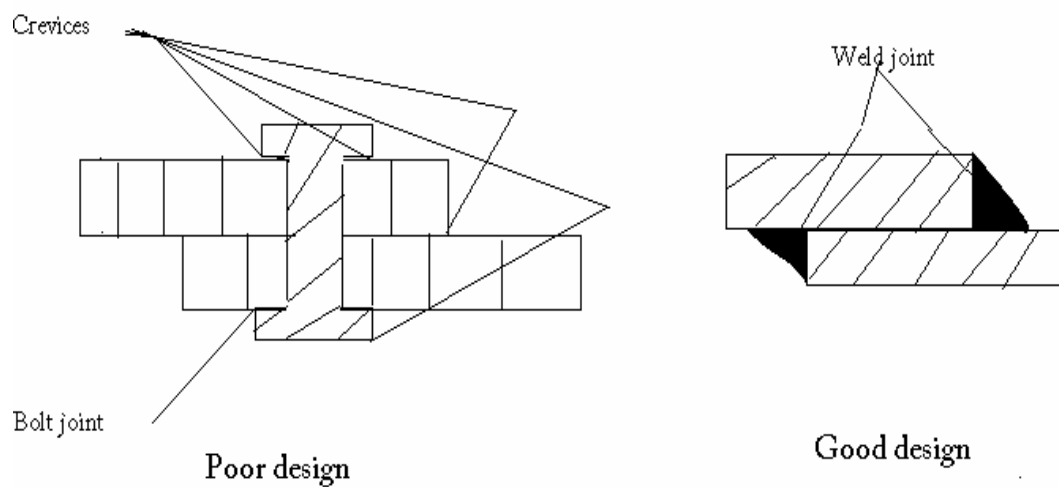
1. The first choice is to use noble metals such as gold and platinum. They are most resistant to corrosion. As they are precious, they cannot be used for general purposes.
2. The next choice is to use purest possible metal. But in many cases, it is not possible to produce a metal of high chemical purity. Hence, even a trace amount of impurity leads to corrosion.
3. Thus, the next choice is the use of corrosion resistant alloys. Several corrosion resistant alloys have been developed for specific purposes and environment. For example, a) Stainless steel containing chromium produce an exceptionally coherent oxide film which protects the steel from further attack. (b) Cupro -nickel (70% Cu + 30% Ni) alloys are now used for condenser tubes and for bubble trays used in fractionating column in oil refineries. (c) Highly stressed Nimonic alloys (Ni -Cr-Mo alloys) used in gas turbines are very resistant to hot gases.

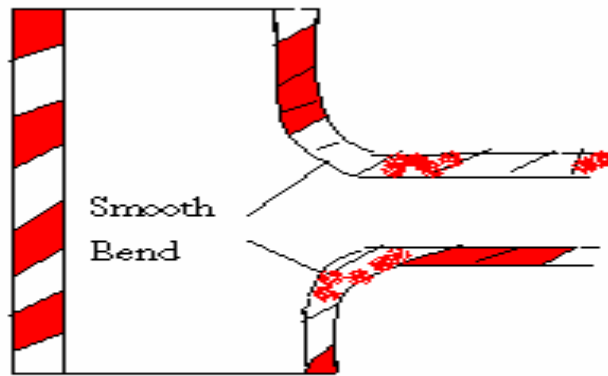
b. Proper Designing:

Proper geometrical design plays a vital role in the control of corrosion of equipments and structures. The general guidelines of the design of materials and components to control corrosion are the following:

- a. Use always simple design and structure
- b. The design must avoid more complicated shapes having more angles, edges, corners etc.
- c. Avoid the contact of dissimilar metals as they may lead to galvanic type corrosion. To overcome this, insulation can be used.
- d. When two dissimilar metals are to be in contact, the anodic area must be as large as possible and the cathodic area should be as small as possible.

- e. As far as possible, crevices (gap or crack) should be avoided between adjacent parts of a structure.
- f. Bolts and rivets should be replaced by proper welding
- g. Metal washers should be replaced by rubber or plastic washers as they do not adsorb water. They also act as insulation.
- h. Corrosion in pipelines can be prevented by using smooth bends.
- i. Heat treatment like annealing minimizes the stress corrosion.
- j. A good design of water storage container is the one from which water can be drained and cleaned easily. Such a design avoids accumulation of dirt etc.



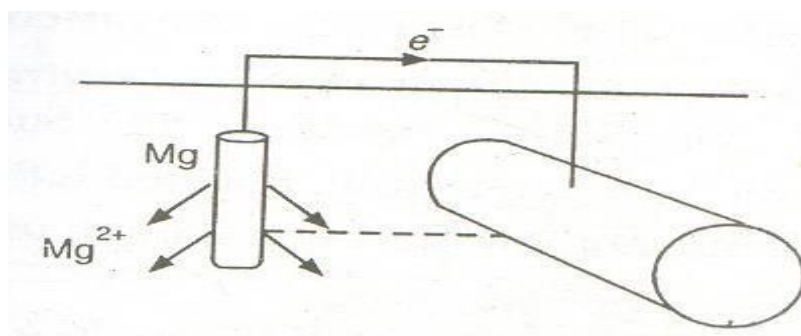


(Best Design)

What is sacrificial anode? Mention its role in control.

1) **Cathodic protection** : The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion doesn't occur. There are two types of cathodic protection.

i) **Sacrificial anodic protection method**: - In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal implies the more active metal itself gets corroded slowly. While the parent structure which is cathodic is protected. The more active metal so employed is called "sacrificial anode" whenever the sacrificial anode is consumed completely. It is replaced by a fresh one. Metal commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Sacrificial anodes are used for the protection of buried pipe lines underground cables, marine structures, ship hulls, water tanks etc.



Sacrificial anode method

- In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.

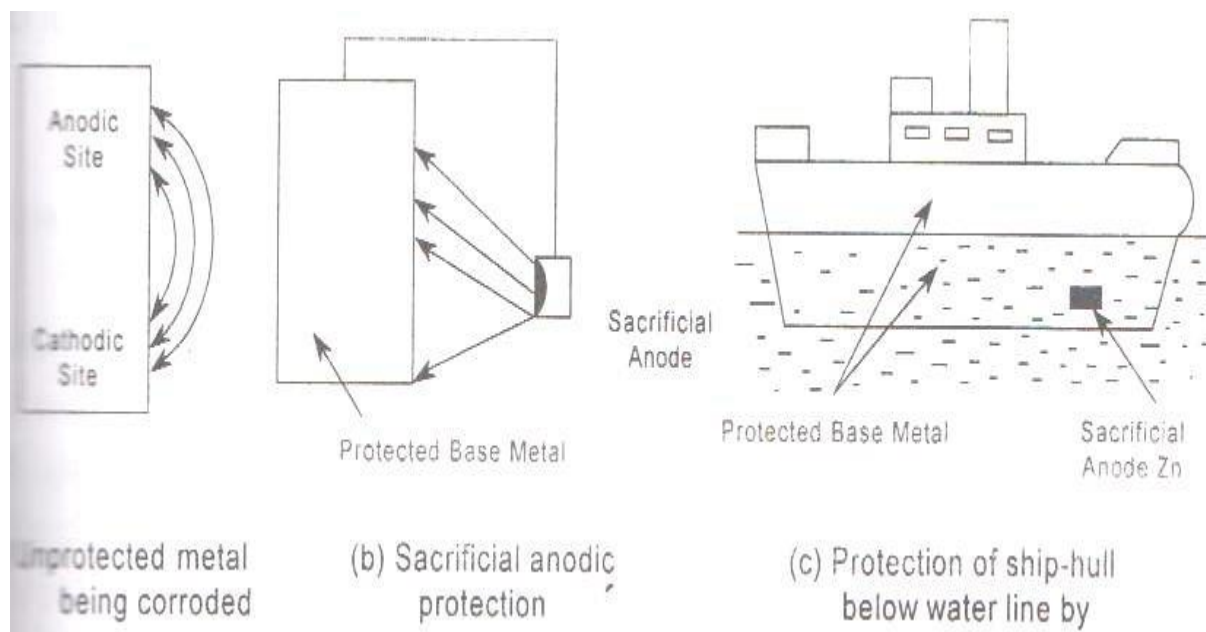
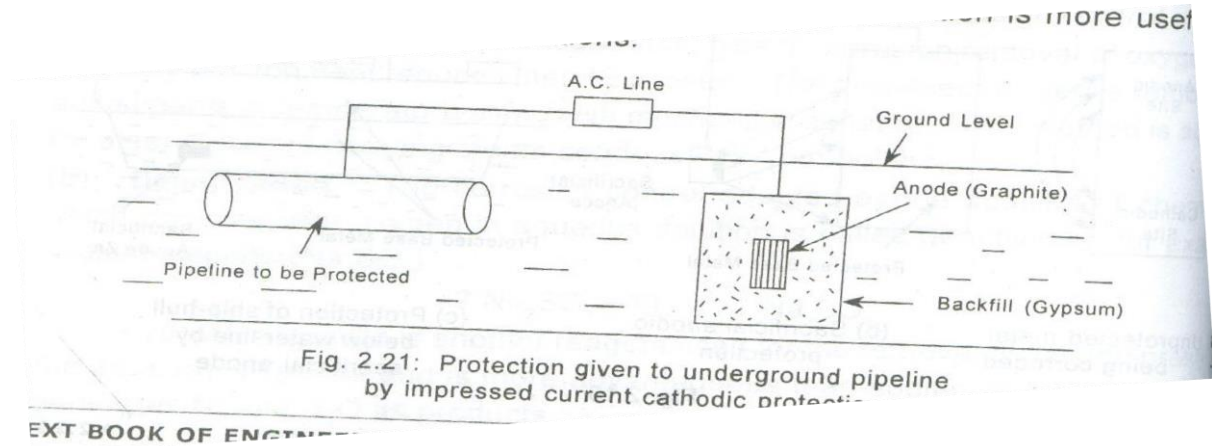


Fig.1.25 Sacrificial anode method: ship hull and underground water pipeline

Impressed current – cathodic protection: -

In this method an impressed current is applied in opposite direction to nullify the corrosion current and current the corroding metal from anode to cathode. Usually the impressed current is derived from a direct current source (like battery or

rectifier on ac line) with an insoluble anode, like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually a sufficient d.c is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected.



The anode is buried in a backfill such as coke breeze or gypsum to increase the electrical contact between itself and the surrounding soil.

Applications:- This type of protection is used in buried structures such as tanks and pipelines, transmission line towers, marine piers, laid up ships etc.,

Advantages: - They can be automatically controlled which reduce maintenance and operational costs.

Metallic coatings:

Methods of application of metallic coatings

1. Hot dipping

- Hot dipping process is applicable to the metals having higher melting point than the coating metal.
- It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer.
- The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Eg. Coating of Zn, Pb, Al on iron and steel surfaces.

The most widely used hot dipping processes are galvanizing and tinning.

Anodic coatings (galvanization):

Galvanizing is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. For carrying out galvanizing firstly the iron or steel article such as sheet, pipe or wire is cleaned by pickling with dil H_2SO_4 solution for 15-20 mts at 60-90°C. In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface. The article is washed well and then dried. It is then dipped in bath of molten zinc maintained at 425- 430°C. The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath. It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness then it is annealed and finally collected slowly.

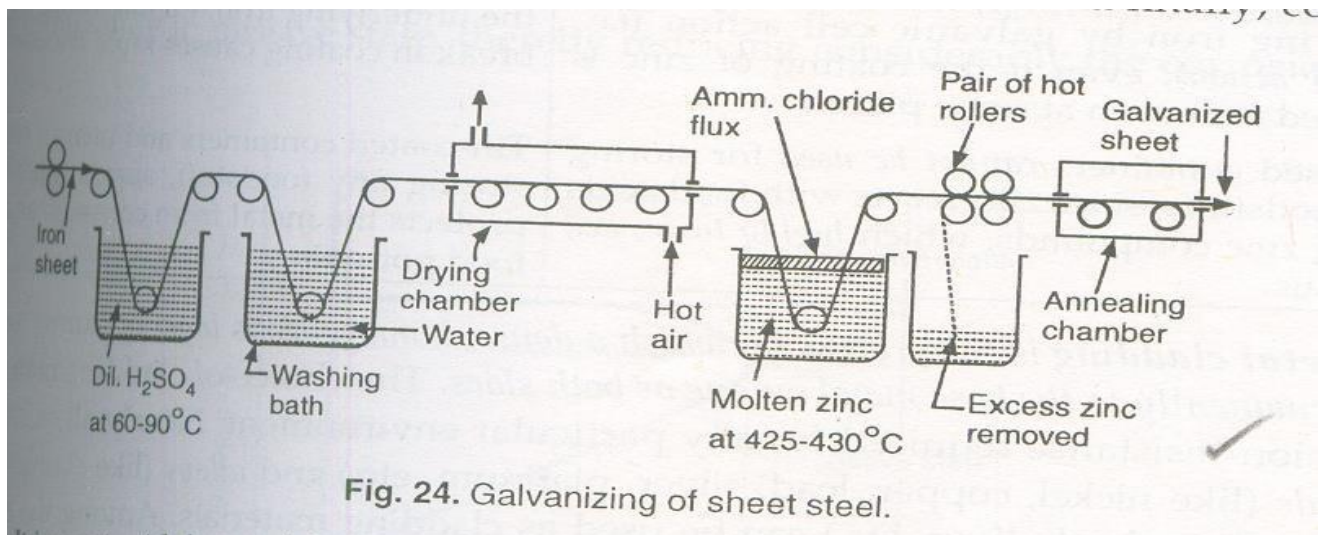


Fig.1.27 Galvanising

Uses: - Roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. which are made of iron are protected from atmospheric corrosion by galvanizing them. But galvanized utensils cannot be used for preparing and storing food stuffs, especially acidic ones since zinc gets dissolved in all acids forming highly toxic compounds.

b. Tinning:

- The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.

- Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.
- A cleaned iron sheet is passed through a bath ZnCl_2 molten flux followed by molten tin and finally through a suitable vegetable oil. The ZnCl_2 flux helps the molten metal to adhere to the base metallic surface.
- . Palm oil protects the tin coated surface against oxidation. Tinning of mild steel plates is done mostly for the requirements of the food stuff

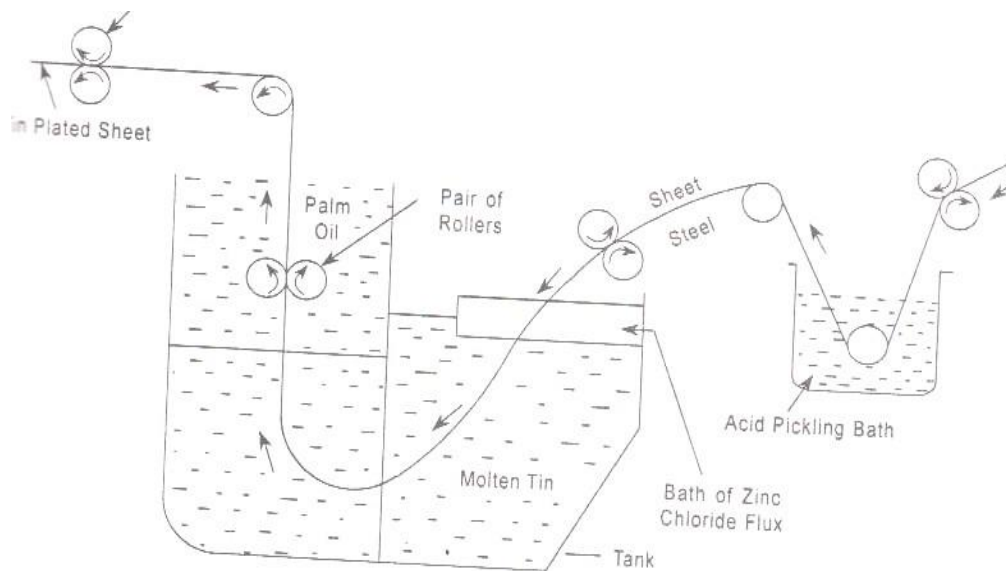


Fig.1.28 Tinning

Electro less plating: A technique of depositing of noble metal on a catalytically active surface of a less noble metal by employing a suitable reducing agent without using electrical energy



Preparation of active surface of the objective to be plated:

Etching: By acid treatment

Electroplating a thin layer: Heat treatment

Treatment with SnCl_2 & PdCl_2 :

Plating bath is composed of :

- (i) Soluble salt of metal: Cl^- & SO_4^{2-}
- (ii) Reducing agents : Formaldehyde & Hypophosphite
- (iii) Complexing agent: Tartarate, citrate, succinate
- (iv) Stabilizer: Thiourea, Lead, Calcium, Thallium etc.,
- (v) Buffer: Sodium acetate and sodium hydroxide and rochelle salt

Examples

Electro less nickel plating::

Pre-treatment of activation of the surface:

The surface to be plated is first degreased organic solvents followed by acid treatment

(ii) Metals and alloys like Al, Cu , Fe etc.

(iii) Activation of di. H_2SO_4

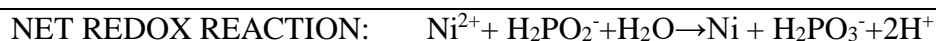
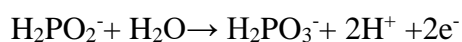
COMPOSITION OF BATH:

Coating solution NiCl_2 (20g/l): reducing agent-sodium hypophosphite (20g/l):

buffer-sodium acetate (10 g/l): Complexing agent- Sodium succinate (15 g/l)

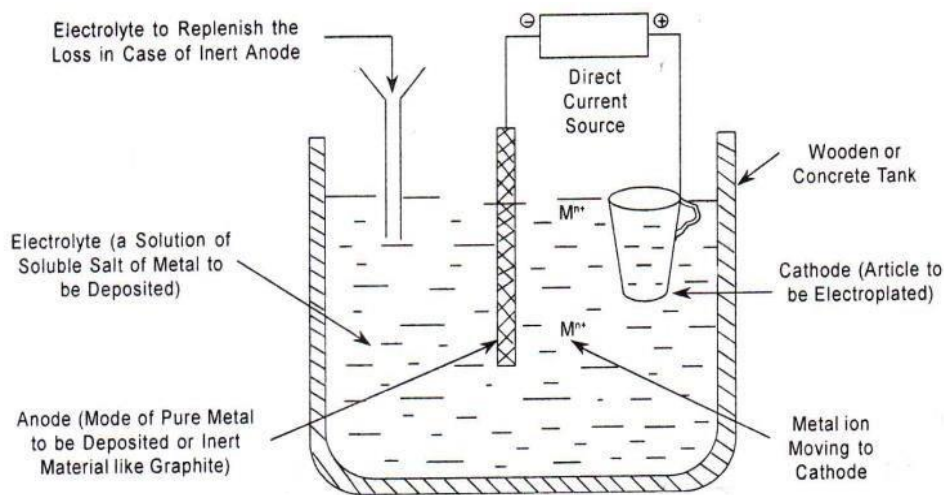
Optimum Ph-4.5: optimum temperature- 93°C

REACTIONS:



Electroplating:

- It is a process in which coating metal is deposited on the base metal by passing direct current through an electrolytic solution containing the soluble salt of the coating metal.
- The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.



- When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.
- Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

Objectives of Electroplating

1. To increase resistance to corrosion, chemical attack and wear resistance of the plated metal
2. To improve physical appearance and hardness
3. To increase the decorative and commercial values of metals
4. To increase the strength of non-metals like plastics, wood and glass etc.
5. To make surface conductive by using light weight non-metallic materials like wood and plastics

Electroplating-Copper plating:

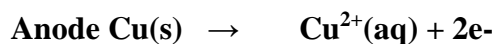
For example, for electroplating of copper on iron article the following are maintained

Electrolytic bath solution: CuSO_4

Anode: Pure copper Cathode: Base metal article

Temperature: 20-40°C (low temp for brighter and smooth surface) Current density: 20-30 mA/cm²

When direct current is passed, the Cu^{2+} ions migrate to the cathode and deposit on the base metal article.



Q12. What are paints? What are their constituents and uses?

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 paint is applied to a metal surface the thinner evaporates, while the drying oil slowly oxidizes forming a dry pigmented film.

Constituents of paints:-

- i) Pigment: It is a solid substance which is an essential constituent of paint it provides
- ii) Capacity to paints
- iii) Strength to paint
- iv) desired colour to paint
- v) Esthetic appeal to the paint film.
- vi) Protection to the paint film by reflecting harmful ultra violet light
- vii) Resistance to paint film against abrasion/wear
- viii) impermeability of paint film to moisture
- ix) increases the weather resistance of the film.

Important pigments used are i) whites – such as white lead, Zinc Oxide, litho phone, titanium oxide.

Red colored – red lead, ferric oxide, Venetian red, chrome red etc. Green colored: - Chromium Oxide

Blue colored: - Prussian blue Black colored: - Carbon black

Brown colored: - Brown umber etc.

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 oils are linseed oil, soya bean oil and castor oil.

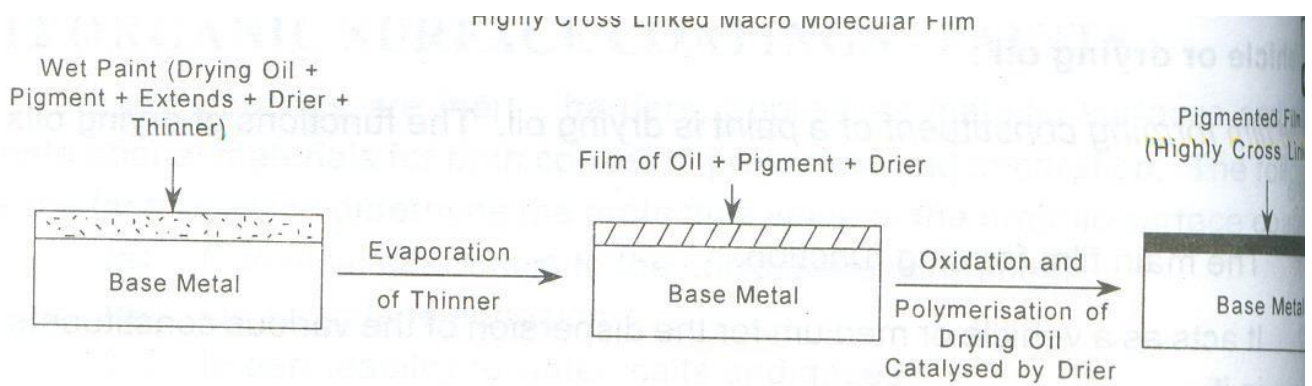


Fig. 2.28 : Drying of paint film

Example of drying oils are

Functions of drying oil: Drying oil supplies i) Main Film-forming constituent ii) Vehicle or medium iii) Toughness iv) adhesion V) Durability and Vi) water proof.

Thinners: i) Reduce the viscosity of the paint to suitable consistency, so that it can easily be handled and applied.

ii) Dissolves the vehicle and the additions increases the penetration power of the vehicle

iii) Helps the drying of the paint film, as they evaporate.

Common thinners are turpentine, benzene, dipentene, naphtha, kerosene etc...

Driers: are oxygen carrier catalysts, they accelerate the drying of the oil film through oxidation, polymerization and condensation. Thus they improve the drying quality of the oil film.

The most effective driers are resonates, lenoleates, tungstates of Co, Mn, Pb and Zinc.

Extenders or fillers: They are added in limited quantities to the oil paints for adjusting the working quantities of the paint they help to present the setting of heavier pigments.

i) They also increase the mechanical strength of the paint film.

ii) They reduce the cost of the paint examples are aluminium silicate, barium carbonate, barium sulphate.

Plasticizers: sometimes plasticizers are added to the paint. They do not evaporate like thinners and they permanently remain in paints.

- i) They improve flexibility and elasticity of the paint film.
- ii) They minimize its cracking

Eg. High molecular weight esters like triphenyl phosphate tributyl phosphate, tricresyl phosphate etc.

Anti-Skinning agents: They are sometimes added to paints to prevent gelling and skinning of the paint film.

Eg. poly hydroxy phenols.

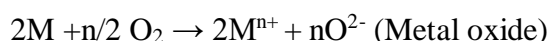
Corrosion: Any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface, is called corrosion.

Examples:-

- i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed.
- ii) Formation of green film of basic carbonate- $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$ on the surface of copper when exposed to moist air containing CO_2

Corrosion is an oxidation process and it is reverse of metal extraction.

The reactions in the oxidation corrosion are:



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 and sulphides.

2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amount of energy.

3. Hence the isolated pure metals are in excited states than their corresponding ores.

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

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

Disadvantages of corrosion: The process of corrosion is slow and occurs only at surface of metals but the losses incurred are enormous. Destruction of machines, equipment, building materials and different types of metallic products, structures etc. Thus the losses incurred are very huge and it is estimated that the losses due to corrosion are approximately 2 to 2.5 billion dollars per annum all over the world.

Theories of corrosion: - Corrosion can be explained by the following two theories .

1. Dry or chemical corrosion.

2. Wet or electrochemical corrosion.

Q1. Explain dry corrosion in detail.

Dry or Chemical corrosion: -

This type of corrosion occurs mainly by the direct chemical action of the environment i.e., by the direct attack of atmospheric gases such as O_2 , halogens, H_2S , SO_2 , N_2 or anhydrous inorganic liquids on the metal surface with which they are in contact. There are 3 main types of chemical corrosion.

1) Corrosion by oxygen (or) oxidation corrosion.

2) Corrosion by other gases like SO_2 , CO_2 , H_2S and F_2 etc.

3) Liquid metal corrosion.

Wet Corrosion or Electrochemical Corrosion

- The direct chemical action of environment on the surface of metal in presence of conducting liquid with the formation of electrochemical cells.
- It a common type of corrosion which occurs usually in aqueous corrosive environment
- Occurs when metal comes in contact with a conducting liquid.
- Formation of galvanic cell on the surface of metal generating anodic and cathodic areas
- At anode oxidation takes place liberating electrons.

- Electrons at anode are transported to cathodic area where H^+ or O_2 and H_2O consumes the electrons generating non-metallic ions like OH^- or O^{2-}
- Metallic (M^+) and non metallic (OH^- or O^{2-}) diffuse towards each other and results in the formation of corrosion product in between the anodic and cathodic area.

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.

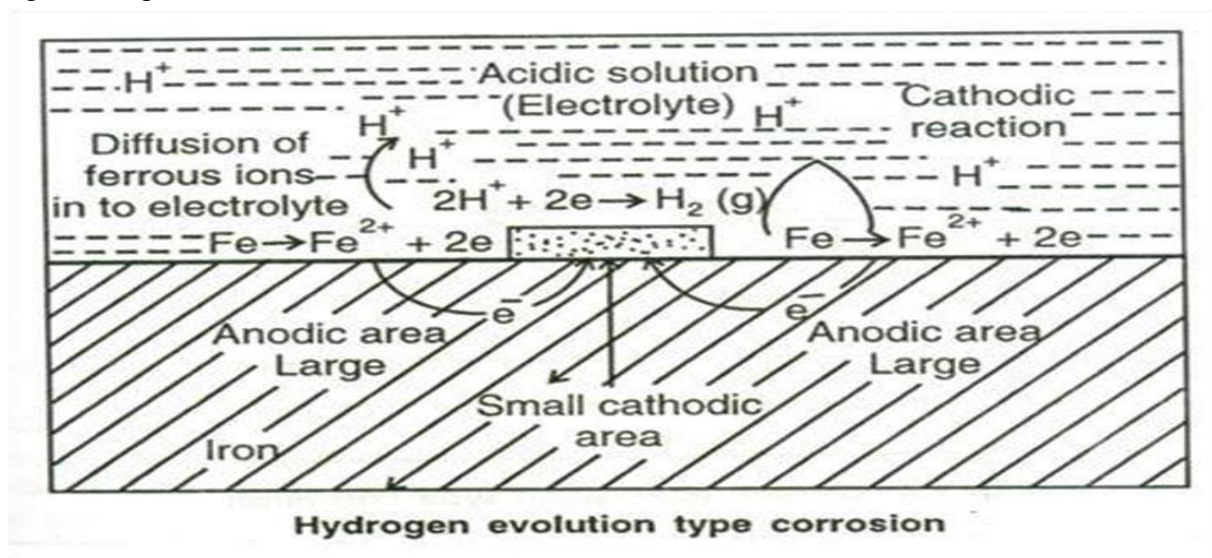
Wet corrosion takes place in two ways.

1. Evolution of Hydrogen
2. Absorption of Oxygen

Evolution of Hydrogen:

This type of corrosion occurs in acidic medium.

Eg: Rusting of iron



At Anode dissolution of iron to ferrous ion takes place with the liberation of electrons

Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)

The electrons released at anode flow through the metal from anode to cathode, where as H^+ ions of acidic solution take up these electrons and eliminated as hydrogen gas

Cathode: $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (Reduction)

The overall reaction is: $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2 \uparrow$

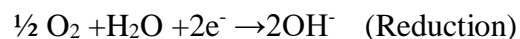
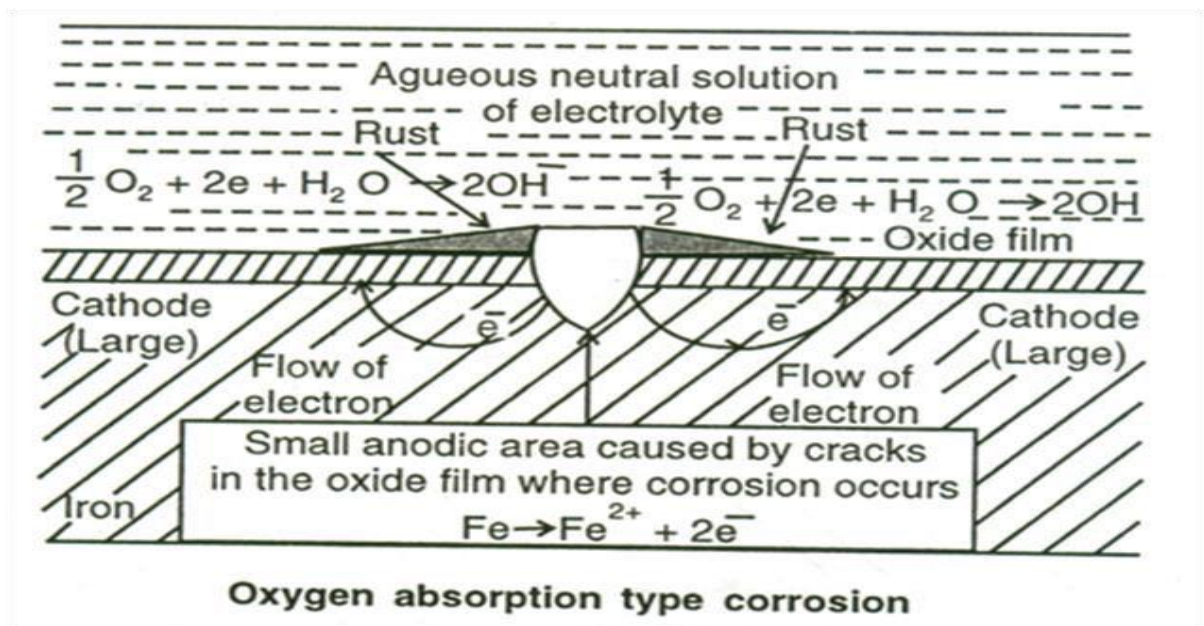
This type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions.

In hydrogen evolution type corrosion, the anodic areas are large and cathodic areas are small.

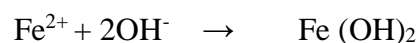
Absorption of Oxygen:

- This type of corrosion takes place in basic or neutral medium in presence of oxygen.
- For example, rusting of iron in neutral or basic aqueous solution of electrolyte 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 and the rest of the metal surface acts as cathodes.
- It shows that anodic areas are small and the cathodic areas are large.

Anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation)



The Fe^{2+} ions and OH^- ions diffuse and when they meet, ferrous hydroxide is precipitated.



If enough oxygen is present, ferrous hydroxide is easily oxidised to ferric hydroxide

