

## **MODULE -2**

### **CORROSION & ITS CONTROL**

#### **CORROSION:**

Corrosion is defined as *“The destruction of metals or alloys by the surrounding environment through chemical or electrochemical changes.”*

The primary factors that initiate corrosion on metals or alloys are atmospheric air, water and also conducting surface of the metal or alloys.

Examples:

- Rusting of iron – a reddish brown scale formation on iron and steel objects. It is due to the formation of hydrated ferric oxide.
- Green scales formed on copper vessels, due to the formation of  $(\text{CuCO}_3 + \text{Cu(OH)}_2)$

#### **Dry Corrosion** (Chemical corrosion)

If the corrosion takes place due to direct chemical attack (in the absence of moisture) that type of corrosion is known as dry corrosion. Chemical corrosion occurs due to the direct chemical reaction between the metal and the gases present in the corrosion environment. Reaction of corrosive gases such as HCl, H<sub>2</sub>S, NH<sub>3</sub> with metal and alloy takes place.

#### **Electrochemical corrosion** (Wet corrosion)

If the corrosion of metal or alloys takes place due to electrochemical attack in presence of moisture or a conducting medium such corrosion is known as wet corrosion or electrochemical corrosion. This process can be explained on the basis of electrochemical theory of corrosion.

#### **Electrochemical theory of corrosion**

Electrochemical theory of corrosion can be explained taking iron as an example.

When a metal like iron is exposed to the environment according to electrochemical theory corrosion of metal takes place due to the formation of anodic and cathodic regions on the same metal surface or when the two metals are in contact with each other in a corrosive medium.

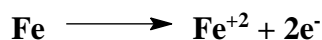
Following are the changes occurring.

- i) Formation of galvanic cells. Anodic and cathodic areas are formed resulting in minute galvanic cells.
- ii) At anode oxidation takes place so that metal is converted into metal ions with the liberation of electrons and move towards cathode.

- iii) Oxygen of the atmosphere is reduced to  $\text{OH}^-$  ions in the presence of water (moisture) at the cathodic area.

### **Anodic reactions**

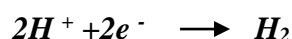
At the anodic area, oxidation of metal iron takes place resulting in the corrosion of iron.



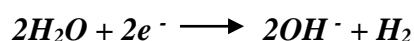
### **Cathodic reactions:**

(i) *In absence of Oxygen*

If the medium is acidic,

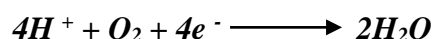


If the medium is neutral or alkaline,



(ii) *In presence of Oxygen*

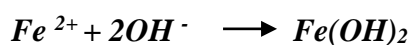
If the medium is acidic,



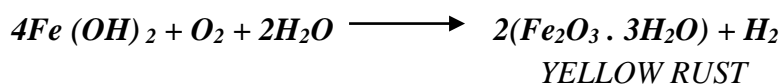
If the medium is neutral or alkaline,



The metal ions ( $\text{Fe}^{2+}$ ) liberated at anode and some anions ( $\text{OH}^-$ ) formed at cathode diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and cathode as



In an oxidizing environment, the insoluble  $\text{Fe}(\text{OH})_2$  oxidized to ferric oxide as following reaction.



If the concentration of oxygen is limited then  $\text{Fe}(\text{OH})_2$  is converted into magnetic oxide of Fe and is known as black rust.

### **Factors affecting the rate of corrosion**

Several factors affecting the rate of the corrosion, which can be divided into two parts

- (i) *Primary factors which are related to metal*
- (ii) *Secondary factors are the environmental factors.*

(i) Primary factors• ***Nature of the corrosion product***

If the corrosion product formed on the surface, is stable, highly insoluble and non-porous in nature with low ionic conductivity then that type of product layer effectively prevents further corrosion, which acts as a protective film.

For E.g., Al, Cr, Ti develops such a layer on their surface and become passive to corrosion.

If the corrosion product formed on the metal surface is soluble, unstable and porous in nature and have good ionic conductivity, they cannot control corrosion on the metal surface.

For E.g., oxide layer formed on metals like Zn, Fe, and Mg etc.

• ***Ratio or size of Anodic and Cathodic area***

The rate of the corrosion is greatly influenced by the relative sizes of cathodic and anodic areas.

If the metal has smaller anodic area and larger the cathodic area and exposed to corrosive atmosphere, more intense and faster is the corrosion occurring at anodic area because rate of anode reaction is greater. At the cathode these electrons are consumed rapidly.

If the cathode is smaller, consumption of electrons will be slower and as a result, corrosion will be slower. For E.g., If tin (Sn) coated on iron (Fe) and in that some areas are not covered or some pin holes are left, there forms smaller anodic area and larger cathodic area because tin is cathodic with respect to iron so intense localized corrosion takes place.

(ii) Secondary factors► ***P<sup>H</sup> of the medium:***

Higher the acidic nature (low pH) of the environment, higher is the rate of corrosion.

If the pH is greater than 10 corrosion of iron is very less due to the formation of protective coating of hydrous oxides of iron.

If pH is between 10 & 3, then presence of oxygen is essential for corrosion of iron. If the pH is lower than 3, severe corrosion occurs in the absence of air due to the continuous evolution of H<sub>2</sub> at cathode. However, metals like Al, Zn etc undergo fast corrosion in highly alkaline medium.

► **Temperature:**

On increasing the temp rate of corrosion process also gets increases because on increase of temp, conductance of the aqueous medium increases hence rate of diffusion also increases.

► **Conductance of medium:-**

Presence of conducting species in the atmosphere increases the corrosion rate. The rate of corrosion in a dry atmosphere is less than that in a wet atmosphere.

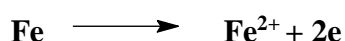
**Types of corrosion**

Corrosion on the metals taking place depending on the nature of metals and depending on the types of environment by different mechanisms, giving different types of corrosion

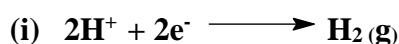
**1. Galvanic corrosion or Differential metal corrosion**

This occurs when two dissimilar metals are in contact with each other in a corrosive conductive medium. The two metals differ in their tendencies to undergo oxidation. The metal with lower electrode potential or more active metal acts as anode and the metal with higher electrode potential acts as cathode. The potential difference is main factor for corrosion to take place. The anodic metal undergoes corrosion whereas cathodic metal gets un-attacked.

Eg: When iron contact with copper, iron has lower electrode potential acts as anode and undergoes oxidation and copper act as cathode remains unaffected.



At the cathode: Depending on the nature of the corrosion environment the cathode reaction is either hydrogen evolution or oxygen absorption.



**2. Differential aeration corrosion:**

Differential aeration corrosion occurs when a metal surface is exposed to differential air concentrations or oxygen concentrations, the part of the metal exposed to higher oxygen concentration acts as cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region. As a result the part of the metal exposed to lower oxygen concentration undergoes corrosion.

At the Anode,  $M \longrightarrow M^{+n} + ne^-$  (oxidation)

At the Cathode,  $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$  (reduction)

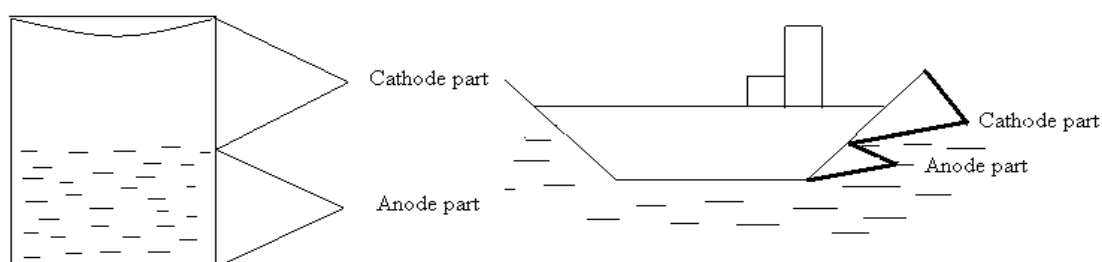
E.g., Part of the nail inside the wall which is exposed to lower oxygen concentration than the exposed part undergoes corrosion.

**Pitting corrosion** and **waterline corrosion** are the two cases of differential aeration corrosion.

**(a) Water line corrosion**

Water line corrosion is observed in steel water tanks, ocean going ships etc.

The water line corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below the water line is exposed only to dissolved oxygen while the part of the metal above the water is exposed to higher oxygen concentration of the atmosphere. Thus part of the metal below water acts as anode and undergoes corrosion and the part above the water line is free from corrosion.



**(b) Pitting corrosion**

Pitting corrosion is a localized and accelerated corrosion resulting in formations of pits or holes. When a small particle of dust, sand or mud get deposited on a metal (like steel). The metal below the deposit is exposed to lower oxygen concentration, acts as anode and undergoes corrosion. The metal surrounding the deposit acts as cathode because it is exposed to higher concentration of oxygen. The portion covered by the dust will not be well-aerated area compared to the exposed surface hence the covered surface becomes anodic with respect to the surface exposed. In presence of an conducting medium (moisture) corrosion starts below the dust part and forming a pit. Once pit is formed the ratio of corrosion increases, because of the formation of smaller anodic and larger cathodic area intense corrosion takes place.

**Corrosion control**

**i) Metal coating**

Corrosion of metals can be controlled by depositing a protective metal over the surface of a base metal. This process is called metal coating.

**Anodic metal coating**

*Anodic coatings are produced by coating a base metal with more active metals which are anodic to the base metal.*

For example, iron is coated with more active metals such as zinc or magnesium, the characteristic feature of anodic coating is that, the base metal on which coating is done will not get corroded even if the coating is ruptured. The exposed surface of the metal is cathodic with respect to the coating metal and the coating metal undergoes corrosion. Therefore, anodic coating is also known as *sacrificial coating*. Galvanization is an example of anodic metal coating.

**Galvanization**

*Galvanization is a process of coating a base metal surface with zinc metal.* Galvanization is carried out by hot dipping method. The galvanization process involves the following steps.

- The metal surface is washed with organic solvents to remove organic matter on the surface.
- Rust and other deposits are removed by washing with dilute sulfuric acid.
- Finally the article is washed with water and dried.
- The article is then dipped in a bath of molten zinc, maintained at 425- 430°C and covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.
- The excess zinc on the surface is removed by passing through a pair of hot rollers, which wipes out excess of zinc coating and produces a thin coating.

**Application:** Galvanized articles are mainly used in roofing sheets, fencing wire, buckets, bolts & nuts etc.

**ii) Anodizing - Anodizing of Aluminium**

*Anodizing is the process of oxidation of outer layer of metal to its metal oxide by electrolysis.* Oxide layer formed over the metal itself act as a protective layer. Anodizing usually carried out in non-ferrous metals like Al, Cr, Ni, etc or their alloys by anodic oxidation process in which base metal is made as anode, in an electrolytic bath of suitable composition and by passing direct current. The most commonly used baths are chromic acid, sulphuric acid or their mixtures. After anodizing, the oxide coating is sealed by immersing in boiling water.

- a) The article to be anodized is degreased, thoroughly polished, connected to the anode and steel or copper is made as the cathode.

- b) The electrolyte is 5-10% chromic acid. The temperature of the bath is maintained at 35°C.
- c) The voltage is programmed to increase from 0 to 50V to maintain an anode current density of 10-20 mA/cm<sup>2</sup>.
- d) During the first 10 minutes, the potential is increased from 0 to 40V.
- e) When the potential reaches 40V, anodizing is continued for 20 minutes.
- f) After 20 minutes the voltage is increased from 40 -50V and held at 50V for five minutes. An opaque oxide layer (some time porous) of 2-8μm thickness is obtained.
- g) The article is dyed properly by immersing for about 20 minutes in an aqueous solution of the dye stuff at 50-60°C.
- h) Finally the object is subjected boiling water treatment, where Al<sub>2</sub>O<sub>3</sub>. H<sub>2</sub>O is formed, which occupies larger volume; hence, pores will be sealed.

Applications: Anodized articles are used as soap boxes, Tiffin carriers

### **Cathodic protection**

*It is a method of protecting a metal from corrosion by converting it completely in to cathode & no part of it is allowed to act as anode.* Corrosion of metals occurs because of the flow of electrons from the anodic to cathodic regions. The anodic regions undergo corrosion whereas the cathodic regions are unaffected. The principle of cathodic protection is to reverse this flow of electron. This can be achieved by providing electrons from an external source so that the metal always remains cathodic.

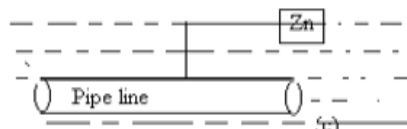
Cathodic protection can be achieved by the following methods.

- (i) Sacrificial anode method
- (ii) Impressed current method

#### **a) Sacrificial anode method**

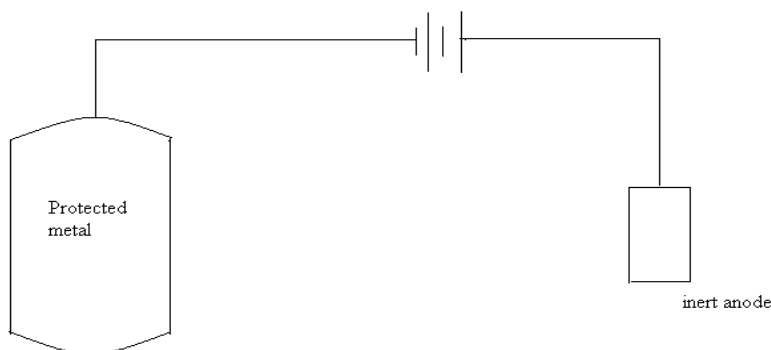
In this method, the metal to be protected is converted completely into a cathode by connecting it to a more active metal. This active metal such as Zinc and Magnesium are the commonly used anodes. These metals, being more active, act as anode and undergo preferential corrosion, protecting the metal structure. Since the anodic metals are sacrificed to protect the metal structure, therefore the method is known as sacrificial anode method. The sacrificial anodes which get corroded in course of time have to be replaced.

- 1) Mg bars are fixed to the sides of ocean-going ships to act as sacrificial anodes.
- 2) Zn wire buried along the oil pipeline.



### b) Impressed current method

Another method of cathodic protection is by the use of impressed current on the metal. The electrons for protection are supplied by a source of direct current. The metal to be protected is made cathodic by connecting it to the cathode of the external source of current (negative terminal of a d.c source). The anode of the source (positive terminal) is connected to an inert electrode. The metal being cathode does not undergo corrosion. Anode being inert remains unaffected. This technique is used to protect marine structure, water storage tanks and other gas or oil pipelines. This method is simple, can protect large metal area with low maintenance cost but expensive, because it needs high current.



### Corrosion penetration rate (CPR)

The corrosion penetration rate (CPR) is defined in three ways:

- The speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment.
- The amount of corrosion loss per year in thickness.
- The speed at which corrosion spreads to inner portion of the material.

The speed or rate of deterioration depends on the environmental conditions and the type and condition of the metal under study.

The CPR is calculated as follows:

$$\text{CPR} = (k \times W) / (D \times A \times T)$$



where  $k = A$  constant

$W$  = total weight lost after exposure

$T$  = time taken for the loss of metal

$A$  = the surface area of the exposed metal

$D$  = the metal density in  $\text{g/cm}^3$

The corrosion penetration rate (CPR) is best expressed in terms of thickness loss of material per unit time. It is expressed in *mpy* (mils per year) or *mm/year* (millimeter per year).

This method involves the exposure of a weighed piece of test metal or alloy to a specific environment for a specific time. This is followed by a thorough cleaning to remove the corrosion products and then determining the weight of the lost metal due to corrosion.

## **QUESTION BANK**

1. *What is corrosion? Explain electrochemical theory of corrosion.*
2. *Explain following types of corrosion. i) Galvanic corrosion or differential metal corrosion. ii) waterline corrosion*
3. *What is anodizing. Explain anodizing of aluminum.*
4. *Explain galvanization?*
5. *Discuss sacrificial anode and impressed current method of corrosion control.*
6. *Explain pitting corrosion.*
7. *Explain the influence of following factors on corrosion.*
  - i) *Nature of corrosion product*
  - ii) *Ratio of Anodic and cathodic area*
  - iii) *temp*
  - iv) *pH*

## **METAL FINISHING:**

### ***INTRODUCTION***

The materials such as metals/alloys are required for various engineering applications.

These materials should be ideal and must meet several requirements like resistance to corrosion, wear resistance, mechanical properties, etc. It is impossible to have all these properties in a single metal. Hence, to improve the lacking properties in these materials, metal finishing is one of the methods employed for the purpose.

Egs: electroplating of metals, electro less plating, chemical conversion coating etc

*Definition: Metal finishing is the process carried out to modify the surface properties of a metal by deposition of a layer of another metal, a polymer or by formation of oxide film.*

### **TECHNOLOGICAL IMPORTANCE OF METAL FINISHING**

- Higher corrosion resistance
- Improved wear resistance
- Provide electrical and thermal conducting surface
- Impart thermal resistance
- Impart solder ability
- Impart hardness
- Provide optical and thermal reflectivity
- In manufacturing electrical and electronic components such as printed circuit boards, capacitors, conductors, etc.

### **ELECTROPLATING:**

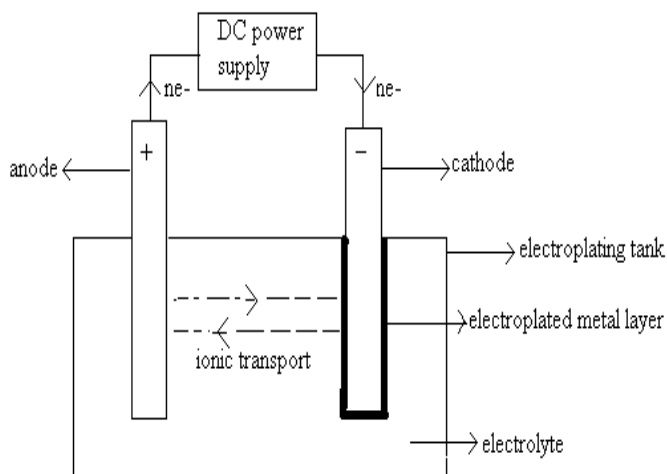
*Defn: It is a process in which a base metal is coated with a thin and uniform layer of another suitable metal by electrolytic deposition.*

It consists of a process in which a metal is deposited on other metal or alloy by passing a direct current through an electrolyte containing the metal ions to be deposited. The common coating metals are Zn, Cu, Ni, Cr, Ag, Au etc.

The electroplating device is an electrolytic cell, in which 2 electrodes, anode and cathode are dipped in an electrolyte solution. The essential components are,

1. An electroplating bath containing a conducting salt and the metal to be plated in a soluble form, as well as the buffer and additives.
2. Electronically conducting cathode, i.e. the article to be plated.

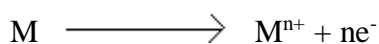
3. The conducting anodes, i.e. the coating metal itself or an inert material of good conductivity like graphite.
4. An inert vessel to contain the above materials, made up of rubber lined steel or plastic, concrete or wood.
5. DC electrical power source.



Electroplating is a process of electrolytically depositing a layer of metal onto a surface. The object to be plated is made cathode in an electrolytic bath containing metal ions  $M^{n+}$ , so that the reaction at cathode is,



Anode reaction is dissolution of same into metal ions in solution.



Hence there is a continuous replenishment of electrolyte during electrolysis. If the anode is inert, that does not go into solution, and then electrolytic salt is added continuously in order to maintain optimum metal ion conc in solution.

Since the process of electroplating involves electrolysis, three factors govern the process of electrolysis. i.e Polarization, Decomposition potential and Over voltage.

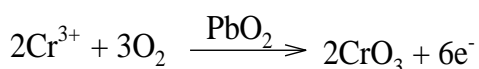
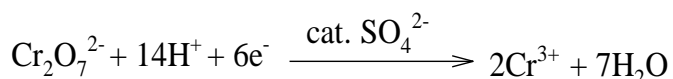
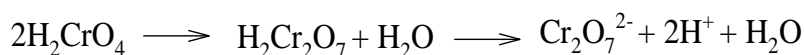
### **Electroplating of Chromium:**

Cr is widely used metal for electroplating. Two forms of Cr are used – Decorative chromium and & Hard chromium.

A thin deposit of chromium (0.25-0.75  $\mu\text{m}$ ) is applied over nickel under undercoat in *decorative coating*. Decorative chromium plating provides a durable coating with a pleasing appearance. In *hard coating* involves thick deposit of chromium directly over substrate. The thickness range is 2.5-300  $\mu\text{m}$ .

<i>Constituents</i>	<i><u>Hard chromium</u></i>	<i><u>Decorative chromium</u></i>
<i>Bath composition</i>	250 g of chromic acid+2.5 g of Sulphuric acid per ltr of the soln(100:1)	250 g of chromic acid+2.5 g of Sulphuric acid per ltr of the soln(100:1)
<i>Temperature</i>	45-55 C°	45-55 C°
<i>Current density</i>	290-580 A/ft <sup>2</sup>	145-430 A/ft <sup>2</sup>
<i>Current efficiency</i>	17-21%	10-15%
<i>Anode</i>	Insoluble anode- Pb/Sb	Insoluble anode- Pb/Sb
<i>Cathode</i>	Article to be plated	Article to be plated

The mechanism of chromium plating is explained as follows.



The plating bath contains  $\text{CrO}_3$  in which Cr is in +6 oxidation state. This is reduced to +3 oxidation state in the presence of  $\text{SO}_4^{2-}$  furnished by  $\text{H}_2\text{SO}_4$ .  $\text{Cr}^{3+}$  ions are reduced to elemental Cr which gets deposited on the surface of cathode. However, the amount of  $\text{Cr}^{3+}$  ions should be restricted in order to obtain satisfactory deposit. Insoluble anodes like Pb-Sb alloys coated with a layer of  $\text{PbO}_2$  which oxidize  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  are used thus controlling the  $\text{Cr}^{3+}$  concentration.

Cr anodes are not used in Cr plating because,

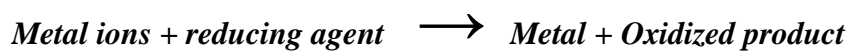
- Cr metal deactivates strongly in acid sulphate medium.
- Cr anode gives rise to  $\text{Cr}^{3+}$  ions on dissolution. In the presence of large conc. Of  $\text{Cr}^{3+}$ , a black Cr deposit is obtained.

Uses:

- Bicycle handles and automobiles.
- Bathroom fittings like taps, showers and dental instruments.

**Electroless plating:** *Electro less plating is controlled deposition of a continuous film of a metal from its metal salt solution on a catalytically active surface of a substrate by a suitable reducing agent, without using electrical energy.* The reduction of metal ions by the reducing agent is catalyzed by the metal atoms being plated. Therefore, electroless plating is also termed as *autocatalytic plating* or autocatalytic redox reaction.

The electro less plating process can be represented as



The surface to be plated should be catalytically active.

- The catalytic metals like Ni, Co, Fe, Pd, Al and Steel do not require any surface preparation before electro less plating.
- Non catalytic metals like Cu, Ag brass etc. need activation. This can be done by passing direct current or by dipping in Palladium chloride – HCl soln.
- Nonconductors like glass, plastics, and ceramics are first activated in a solution of  $\text{SnCl}_2$  & HCl. Then it is immersed in a solution of Palladium chloride and HCl.

**Distinction between Electro plating and Electroless plating:**

	<b><i>Property</i></b>	<b><i>Electro plating</i></b>	<b><i>Electroless plating</i></b>
1.	<i>Driving force</i>	Direct Current	Autocatalytic redox reaction
2.	<i>Anode</i>	Separate anode is needed.	Separate anode is not needed and Catalytically active surface of the substrate act as anode.
3.	<i>Cathode</i>	Object to be plated	Article to be plated which must have a catalytic active surface.
4.	<i>Nature of deposit</i>	Not satisfactory	Well satisfactory.
5.	<i>Applicability</i>	Only to conductors	Both conductors and nonconductors
6.	<i>Reducing agent</i>	Electrons	Chemical reagents.

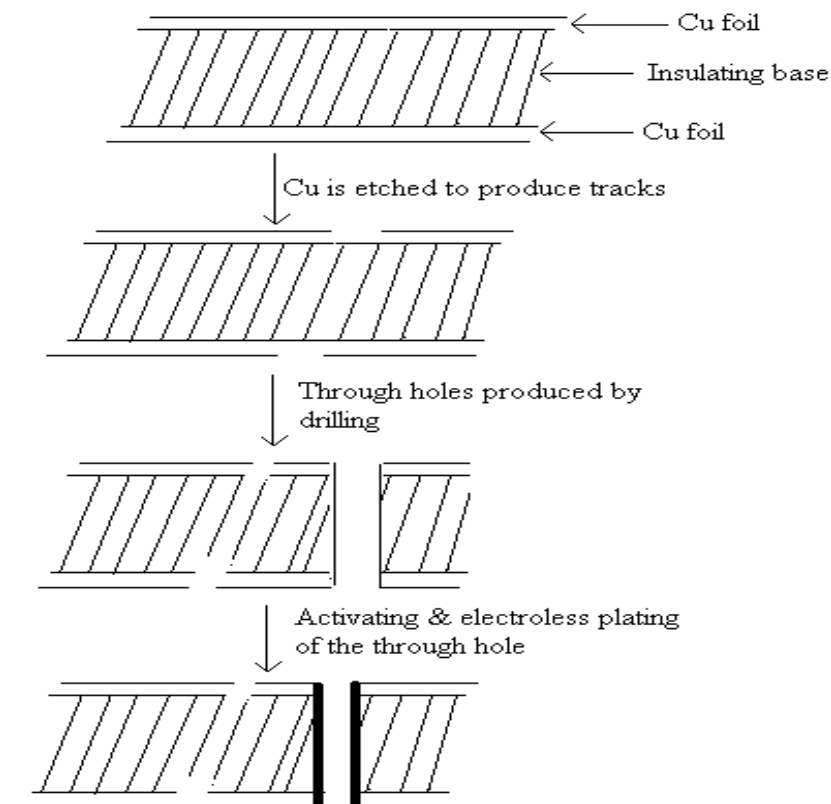
### **Electroless plating of Copper:**

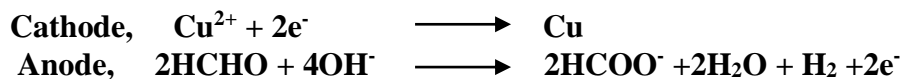
The base object used is a plastic board which is decreased and etched in acid. Then activated by treating with  $\text{SnCl}_2$  in  $\text{HCl}$  solution, followed by dipping in  $\text{PdCl}_2$  solution and dried.

<i>Plating Bath:</i>	$\text{CuSO}_4$ 12g/ltr
<i>Reducing agent:</i>	$\text{HCHO}$ (8g/ltr)
<i>Complexing agent:</i>	EDTA 20g per litre.
<i>Buffer:</i>	$\text{NaOH}$ (15g/L) + Rochelle salt (14g/L)
<i>Stabilizer :</i>	Thiourea (0.1g/L)
<i>pH :</i>	11
<i>Temp :</i>	25°C

For the manufacture of the double sided PCB's, the electric connections between two sides of the board are made by drilling hole & then plating through holes by electroless plating.

The plastic board is initially covered with Cu layers by using thin layers of electroformed Cu foils. Then selected areas are protected by employing electroplated image and the remaining part of the plated copper is etched so as to get required type of circuit pattern (or track). Connection between the two sides of PCB is made by drilling holes, followed by electroless Cu plating through holes.





Applications:

- Mainly used in metalizing printed circuit boards (PCB).
- Plating on nonconductors.
- For decorative plating on plastics.

## **QUESTION BANK**

1. *What is electroplating process? Differentiate between electroless plating and electroplating*
2. *Discuss chromium plating process.*
3. *Explain electro less plating of copper with relevant equations.*
4. *Explain technological importance of metal finishing.*

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