

## 4. Plating Techniques

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**Syllabus:** Introduction: technological importance. Electroplating, principles of electroplating, factors affecting the nature of electro deposit: throwing power, numerical problems on throwing power, electroplating process of gold by acid cyanide bath. Electroless plating; advantages of electroless plating over electroplating. Electroless plating of copper and its application in the manufacture of PCB.

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### Plating or Metal finishing:

The large numbers of metals used in most of engineering works/applications need an ideal metal or alloy which can fulfill all the properties like corrosion resistance, wear and tear resistance, impact resistance, mechanical, electrical and thermal properties, etc., But none of the metals possess all these properties. Metal surfaces are modified in order to satisfy their lacking properties and this surface modification is achieved by the technique known as “**Plating Technique.**”

**Plating or Metal finishing** is a surface process carried out to modify the surface properties of a metal by deposition of a layer of another metal or an alloy or a polymer film. Examples: electroplating of metals, electroless plating, chemical conversion coating etc.

### Technological importance of metal finishing:

Plating technique finds extensive applications in variety of industries, extending to many electronics, engineering and metal processing companies as well as to both large and small specialist firms. The technological importance of plating technique is in imparting certain additional properties to the materials in addition to their intrinsic properties. So that, the utility of the materials is increased. Metal finishing imparts desirable surface characteristics such as,

1. Imparts higher corrosion resistance.
2. Imparts improved wear resistance.
3. Provides decorative appearance.
4. Increase abrasion and impact resistance
5. Improves chemical resistance.
6. Imparting thermal resistance/conducting surface,
7. Increase hardness and improved solderability.
8. Provides optical reflectivity or thermal conducting surface.
9. Manufacturing electrical and electronic components such as PCB, capacitors etc.
10. In electroforming of objects, in electro machining

## 11. In electro polishing and electrochemical etching.

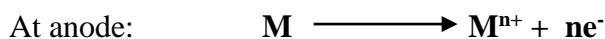
### Electroplating:

It is a process in which a layer of metal is deposited on the surface of another metal by applying electric current. The aim of electroplating is to alter the properties and characters of a surface so as to provide improved appearance, ability to withstand corrosion, enhanced wear and abrasion resistance, good electrical contact etc.

### Theory of Electroplating:

Electroplating is carried out in an electrolytic cell. It consists of two electrodes, the metal to be coated is taken as cathode and connected to negative terminal of a DC power source. Anode is connected to positive terminal of the power source. The electrodes are dipped in an ionic solution of the metal to be plated. On applying direct current, cations move towards cathode and get reduced to metal atoms and deposited over cathode. When a direct current is passed through an electrolyte solution, the following chemical changes take place in the cell.

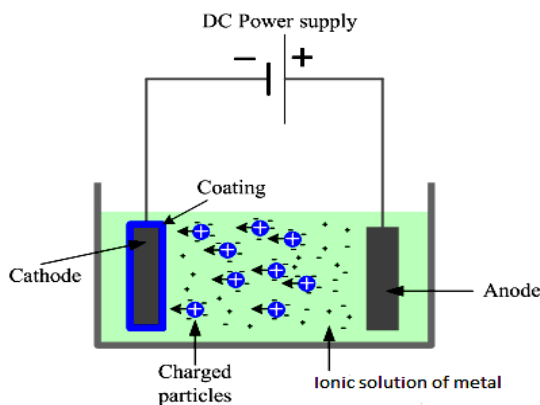
- At anode oxidation takes place producing metal ions into the solution. If the anode is dissolvable, thickness of anode gradually decreases. If the anode is inert one, only chemicals present on the electrode surface are oxidized and anode itself will not react. Here, electrolyte should be added from outside to maintain the cationic concentration and thereby to continue the electrolysis.



- Cations (metal ions) move towards cathode. At the cathodic surface, cations are reduced to metal atoms and get deposited over it. This process of deposition of metal on the cathodic material is called as electroplating. Thus, concentration of cations decreases in the bulk of the solution.



Thus, by the act of an electric current, an electrolyte is decomposed at the surface of the electrodes. This process of decomposition of an electrolyte by passing electric current is called as electrolysis.



**Characteristics of a Good Deposit:**

1. The deposit should be continuous, uniform, non-porous and adhesive.
2. It should be of fine grained nature.
3. It should be bright and lustrous.
4. It should be hard and ductile.

**Principles of electroplating:**

**1) Decomposition Potential ( $E_D$ ):** The minimum potential which must be applied for continuous electrolysis is called as decomposition potential ( $E_D$ ). In an electrolytic cell, the following processes occur during electroplating of metal: i) Cations are attracted towards cathode, ii) Anions are attracted towards anode, iii) Cations are reduced to metal atoms at the surface of cathode, iv) Anions are oxidized at the surface of anode.

Each of these steps has its own potential. If the externally applied potential is less than potential of these processes, then electroplating of metal does not occur. Therefore, electroplating of metal occurs smoothly and continuously when the applied potential is greater than the potential of all these steps.

Decomposition potential is given by the equation:

$$E_D = E_{\text{Back}} + \eta$$

Where,  $\eta$  is the over potential and  $E_{\text{Back}}$  is the back EMF.  $E_{\text{Back}}$  is the back difference in potential of anodic and cathodic reactions occurring in the cell during electrolysis. The EMF opposes the externally applied potential and hence it is called as back EMF.

$$E_{\text{Back}} = E_{\text{cathode}} - E_{\text{anode}}$$

It is more difficult to deposit the metal which has a higher decomposition potential.

**2) Over Potential or Overvoltage ( $\eta$ ):** Over potential is defined as the excess potential which must be applied above the theoretical decomposition potential for continuous electrolysis. In most of the cases, decomposition potential ( $E_D$ ) required carrying out continuous electrolysis is greater than theoretical decomposition potential. This difference between  $E_D$  and theoretical decomposition potential ( $E_{\text{Back}}$ ) is called as over voltage ( $\eta$ ).

Over potential = Experimental decomposition potential ( $E_D$ ) – Theoretical decomposition potential ( $E_{\text{Back}}$ )

$$\text{i.e. } \eta = E_D - E_{\text{Back}}$$

Over voltage is mainly due to polarization of electrodes and other side reactions that occur at the electrode surface during electroplating. One of the main side reactions is liberation of hydrogen at cathode.

**3) Polarization:** During electrolysis, metal ions present at the vicinity of cathode get reduced to metal atoms. Therefore, concentration of metal ions at the vicinity of cathode decreases. To maintain the same concentration, metal ions must be supplied from the bulk of the solution to vicinity of the electrode. If metal ions are not supplied sufficiently, then the concentration of metal ions at the electrode surface decreases. This leads to decrease in the potential of electrode according to Nernst equation.

$$E = E^0 + \frac{2.303RT}{nF} \log [M^{n+}]$$

**This decrease in electrode potential due to insufficient supply of ions from bulk of the solution to surface of the electrode is called as Polarization.** Polarization occurs at anode also. Potential required overcoming polarization of anode and cathode is called as polarization potential. It depends upon, 1) Conductivity of the solution, 2) Current density applied, 3) Temperature, 4) Rate of stirring of the electrolyte solution, 5) Nature of the electrode.

Effect of polarization can be minimized by stirring the electrolyte continuously, by using electrodes of larger surface area and electrolytes of higher conductivity.

### **Factors influencing the nature of deposit:**

There are several factors, which affects the nature of an electro deposit. They are

1) **Current density:** Current density is the applied current per unit area of the cathode surface. It is usually expressed in mA/cm<sup>2</sup>. At lower current density, few numbers of ions are reduced and atoms find the most favorable position resulting in uniform deposit. But, it may not result in a continuous layer. At a very high current density, large numbers of ions are reduced per unit surface area of the electrode resulting in a non-uniform, bad deposit. At higher current density, release of H<sub>2</sub> gas bubbles leads to brittle or burnt deposit. Therefore, an optimum current density should be experimentally determined and applied to obtain good electro deposit.

2) **Plating bath solution:** Plating bath used in electro plating process mainly contains ionic solution of the metal being coated over the material and other compounds like electrolytes, complexing agents and

organic additives. It is important to monitor the concentration of the various species in the bath to obtain a good deposit.

- i) **Metal ions**: Normally concentration of the metal ions in plating bath should be maintained between  $1-3 \text{ mol/dm}^3$ . Higher concentration increases the mass transfer leading to poor deposit. Lower concentration leads to discontinuous deposit.
- ii) **Additional electrolytes**: These are the compounds added to increase the conductivity of the plating bath solution and cathode efficiency. And also the added electrolyte sometimes acts as a buffer solution.
- iii) **Complexing agents**: Complexing agents are added to convert metal ions into complex ions so as to get a fine-grained and more adherent deposit.

Complexing agents are employed,

1. When the cathode metal and plating metal ions as such are known to react.
2. To maintain the metal ion concentration in the plating bath by converting them into complex ions.
3. To make the potential of the plating metal ions more negative in order to carry out plating at a lower potential.
4. To prevent the passivation of anode and consequent loss of current efficiency.
5. To improve the throwing power of the plating bath.
6. To enhance the solubility of the slightly soluble metal salts.

The most common complexing agents used in electroplating are cyanide, hydroxide and sulphamate ions.

- iv) **Organic additives**: These are the organic compounds added in small quantity to plating bath to modify the structure, morphology and properties of the deposits. There are four classes of organic additives:

**Brighteners**: For a deposit to be bright the microscopic roughness of the deposit should be low compared to the wavelength of incident light so that it is reflected rather than scattered. Brighteners are used in plating bath to obtain bright deposit. Example: Coumarin, thiourea are used in Ni electrodeposition.

**Levellers**: These are used to obtain an even electrodeposit on the irregular surface. These act by getting adsorbed at regions where rapid deposition takes place. Thus adsorption is preferentially at dislocations at peaks. The adsorbed additives reduce the rate of deposition and rate of  $e^-$  by acting as a barrier.

Example: Sodium alkyl sulphonate. Sometimes brighteners also act as levellers.

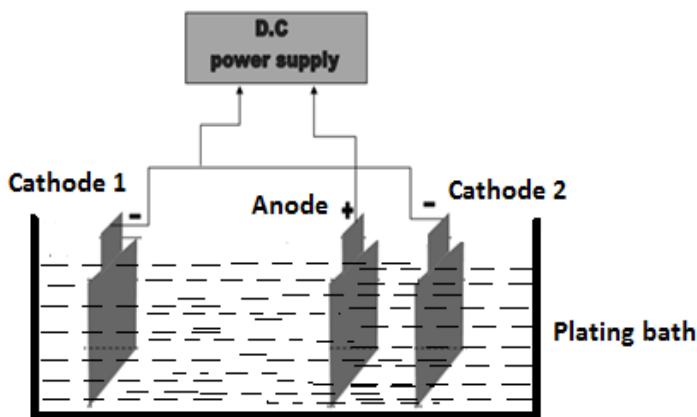
**Stress relievers [Structure modifiers]:** Certain additives change the structure of the deposit and may be even the preferred orientation or the type of lattice. Stress may be due to lattice misfit. The structure modifiers modify the structure of the deposit in such a way as to reduce the internal stress. Example: Saccharin is used as stress reliever in Ni plating.

**Wetting agents:** During electroplating in some cases there is simultaneous deposition of hydrogen and metal at the cathode. The bubbles of hydrogen get trapped within the deposit and try to escape after the plating is over by breaking it. This leads to porous and burnt deposit. Wetting agents effectively release  $H_2$  gas bubbles from the cathodic surface and hence prevent them from entrapment. Example: Sodium lauryl sulphate is used as wetting agent in plating bath of Ni and Zn.

3) **pH of plating bath:** For a good electro deposit, the pH of the bath must be properly maintained. At low pH, evolution of hydrogen at cathode occurs, resulting in a burnt deposit. At high pH precipitation of hydroxides of the metal on the electrode surface occurs. Hence optimum pH range for most plating baths should be from 4 to 8.

4) **Temperature:** Rate of electro deposition increases with increase in temperature. But, at higher temperatures evolution of  $H_2$  gas, corrosion of equipment also increases and organic additives may be decomposed. At lower temperature, rate of electro deposition is lower. Hence, plating is carried out at moderate temperature of 30-60  $^{\circ}C$ .

5) **Throwing power of the plating bath:** The ability of a plating bath solution to produce an even deposit is measured by its throwing power. It is difficult to get electric deposit with uniform thickness on the entire surface especially when the object is complex in nature. Throwing power of plating bath can be determined by using the **Haring-Blum cell**.



The cell contains plating bath solution whose throwing power is to be determined. The two cathodes are placed at markedly different distances  $d_1$  and  $d_2$  where  $d_1 > d_2$  from a single central anode and electroplating is carried out.

The weight of the metal plated on the two cathodes  $W_1$  and  $W_2$  are determined.  $W_1$  is for  $C_1$  and  $W_2$  is for  $C_2$ .

$$\% \text{ throwing power of the bath solution} = \frac{(X - Y) \times 100}{(X + Y - 2)}$$

where,  $X = d_1/d_2$ ,  $Y = W_2/W_1$

When  $W_1 = W_2$  i.e. amount deposited is same irrespective of the placement of the electrode, then throwing power is considered very good (100 %). When the calculated throwing power is  $-100\%$  then it is considered as very poor. Although the TP does not directly determine the nature of the deposit, certain factors which influence the uniformity of the plating is expressed in terms of TP. These include

- (i) **Conductance of the solution:** In a solution of high conductance, the current distribution will be uniform over a complex cathode surface and therefore the rate of deposition is uniform. i.e., Solutions with higher conductivity will have higher TP.
- (ii) **Anodes:** By Optimum Placement of the anodes and use of auxiliary anodes uniform deposition may be achieved.
- (iii) **Complexing agents:** Presence of complexing and addition agents such as levelers improves the throwing power.

**Cleaning of the articles to be plated [Pretreatment of the surface]:** To obtain sound deposit it is essential for the surface to be properly prepared. Commonly, two steps are involved in the cleaning process:

- 1) Grease, dirt, wax, oils present on the surface are removed by washing with organic solvents like 1,1,1-trichloroethane and perchloroethylene.
- 2) The oxide film (rust) present on the surface is removed by pickling in dilute  $H_2SO_4$  for about 5-20 minutes.

Finally, article is rinsed with hot deionized water and dried.

### Requirements of an electrolyte solution for electroplating:

The electrolyte solution used for electroplating should possess the following characteristics.

1. Metal content of the solution should be high and the free metal ion concentration should be relatively low.

2. The conducting power of the solution should be high.
3. It should be stable under the operating conditions, without undergoing hydrolysis, oxidation, reduction, and other chemical changes.
4. The solution should dissolve the anode quite efficiently whenever an active anode is used and should be able to maintain constant metal content of the solution.
5. It should possess good covering power and throwing power. Covering power is the measure of the ability of the bath solution to deposit the metal over the entire surface of an article.

However, no single electrolyte satisfies all these requirements. Therefore, usually, a mixture of two or more electrolytes is used along with suitable addition agents.

$$\text{Cathode efficiency} = \frac{\text{Weight of metal actually deposited}}{\text{Weight of metal calculated from the quantity of electricity passed}} \times 100$$

$$\text{Anode efficiency} = \frac{\text{Weight of metal dissolved}}{\text{Weight of metal calculated theoretically from Faraday's law}} \times 100$$

**Electroplating of Gold:** Gold plating was initially applied for decorative purposes on jewellery articles. But later it is found applications in the industries, for various purposes.

Plating bath used for electroplating of gold is generally called as cyanide bath because cyanide is used as complexing agent.

Constituents	Bath D (Acidic)
(1) Plating bath Solutions:	
(i) Potassium gold cyanide	6.0 – 18.0 g/dm <sup>3</sup>
(ii) Mono potassium dihydrogen phosphate g/dm <sup>3</sup>	20.0 g/dm <sup>3</sup>
(iii) Potassium citrate g/dm <sup>3</sup>	50.0 g/dm <sup>3</sup>
(2) pH	3 – 6
(3) Temperature	40 – 70 °C



(4) Current density	1 – 20 A/ft <sup>2</sup>
(5) Cathode efficiency	80 – 90 %
(6) Anode	Pt, Platinized Ti, Carbon
(7) Cathode	Object to be electroplated (It must be free from dirt. Oil and grease, etc., in order to get a good deposit).
(8) Leveler	Sodium allyl sulphonate

Typically, four bath compositions are used for gold plating. Two of them are alkaline cyanide baths, one is neutral cyanide bath and fourth one is acidic cyanide bath. Rubber or plastic lined tanks can be employed for the plating bath and the temperature being kept below 70°C. Agitation in terms of cathode movement or solution circulation is desirable.

Bath A and B are used primarily for decorative gold plating and for industrial uses. Bath A is used for low thickness of gold (0.02 to 0.25 µm) and bath B is used for large thickness of gold (up to 40 µm for items subject to heavy wear and abrasion). These baths are not suitable for plating on PCBs.

Batch C is used for components where baths A and B cannot be used. The gold deposits from this bath are less porous compared to those from baths A and B. Bath D is similar to bath C in use and yields a gold deposit of 99.999% plus purity with highest ductility. Since insoluble anodes are used in almost all gold baths, gold salt – the potassium gold cyanide complex, is periodically added to replenish the gold.

When gold is directly plated on copper, the copper atoms have the tendency to diffuse through the gold layer, causing tarnishing of its surface and formation of an oxide layer. Therefore, a layer of a suitable barrier metal, usually nickel to be deposited on the copper substrate, before gold plating. The nickel deposit also provides mechanical backing for the gold layer, improving its wear resistance. It also reduces the effect of pores present on the gold layer.

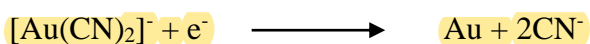
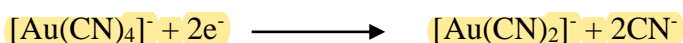
When gold is plated on silver, silver atoms also diffuse through the gold layer, causing gradual fading of its color and tarnishing the surface. This process may take months to years, depending on the thickness of the gold layer. Therefore, it is better to use a barrier metal layer underneath the gold deposit.

**Applications:** Gold deposit is a shiny deposit with good tarnish and corrosion resistance. It has good electrical conductivity, comparable with copper and silver, and has an ability to reflect IR radiation.

1. Used for decorative purposes in jewelers, watch cases, pen points, hallow ware, etc.,

2. In the electrical industry, printed circuits, contacts and connectors are gold plated.
3. In electronics, transistors and integrated circuit parts are gold plated.
4. In the aerospace industry, instrument coverings and external surfaces exposed to radiation in space are gold plated.
5. Reactors and heat exchangers in the conductor tube for desalination are gold plated, because of the high corrosion resistance nature of gold.
6. Because of its acid and corrosion resistance, it is used for decorative purpose especially in tombs of temples.

### **Reactions:**



Gold metal dissolves very fast in cyanides, therefore inert anode is used instead of pure gold metal.

$\text{AuCl}_3$  is periodically added to cyanide bath to maintain the concentration of  $[\text{Au}(\text{CN})_4]^-$ .

Concentration of gold ions should be minimum in plating bath to maintain a good, coherent deposit.

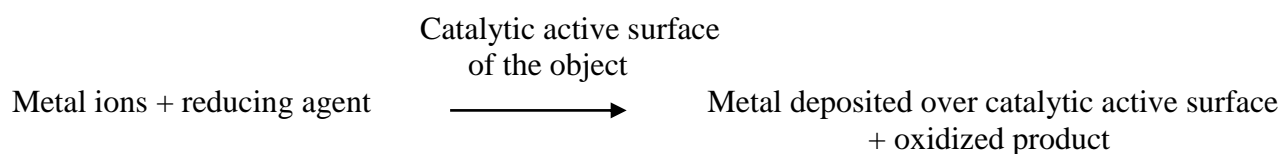
### **Electroless plating:**

Deposition of layer of metal from its salt solution on a catalytically active surface of the object using a suitable reducing agent without using electric current is called electroless plating.

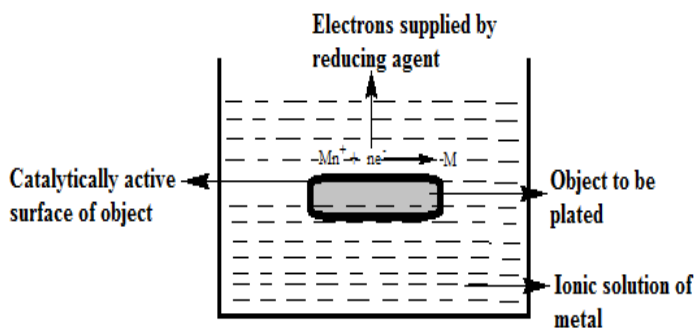
OR

It is a method of depositing a metal or alloy over a substrate (conductor or non-conductor) by controlled chemical reduction of the metal ions 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, electro less plating is also termed as autocatalytic plating.

The electro less plating process can be represented as,



The surface to be plated should be catalytically active. This can be done by dipping in  $\text{SnCl}_2$  containing  $\text{HCl}$  at  $25^\circ\text{C}$  followed by  $\text{PdCl}_2$ .  $\text{SnCl}_2$  reduces palladium ions to deposit small amount of palladium metal on the surface of the material which catalyzes the redox reaction.



### **Composition of electroless plating bath:**

Electro less plating bath will contain the following components.

1. Metal salts to provide metal ions for deposition.
2. Reducing agent for reduction of metal ions to metal atoms. Eg., Formaldehyde, Hypophosphite.
3. Complexing agents to complex metal ions to prevent bulk deposition. Eg., citrate, tartarate, succinate.
4. Stabilizer to give more stability to the solution. Eg., Thiourea and cations of Pb, Ca & Thallium
5. Accelerator to increase the rate of plating. Eg., anions like succinate, glycinate & fluoride.
6. Buffers to control pH.
7. Brighteners.

### **Advantages of electroless plating:**

1. Does not require electrical power source.
2. It is applicable to conductors, semiconductors and non-conductors like plastics.
3. Electro less plating is less porous than electroplates and possess unique characteristic chemical, mechanical and magnetic properties.
4. Electro less plating baths have better throwing power and deposit a more uniform metal coating over an article irrespective of its shape or size.
5. Levellers are not required in electroless plating.
6. Electroless coating will be harder as compared to electroplating coating.
7.  $H_2$  gas is not trapped.

### **Disadvantages of electroless plating:**

1. Rate of deposition is slow.
2. Deposit is contaminated with oxidized product.
3. It generates more waste than any other plating technique.

### Electroless plating of Copper

Electroless plating of copper on PCB's is carried out as follows.

Metal ion solution:	CuSO <sub>4</sub> .5H <sub>2</sub> O (12 g/L)
Reducing Agent:	Formaldehyde (HCHO, 8 g/L)
Buffer	Rochelle salt (sodium potassium tartarate, 14 g/L) + NaOH (12g/L)
Complexing agent:	EDTA (20g/L)
pH :	11 -12
Temperature:	25 °C
<u>Reactions:</u>	
At Anode:	$2\text{HCHO} + 4\text{OH}^- \longrightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$
At Cathode:	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$
Overall reactions:	$4\text{OH}^- + \text{Cu}^{2+} + 2\text{HCHO}^- \longrightarrow \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2$
Applications:	<ul style="list-style-type: none"> <li>• For Producing through – hole connections</li> <li>• Widely used for metalizing printed circuit boards</li> <li>• For plating on non conductors</li> <li>• For decorative plating on plastics.</li> <li>• As an undercoat/base for electroplating.</li> </ul>

### Electroless plating of copper in the manufacturing of PCBs:

The surface to be coated is first degreased by organic solvents or alkali followed by acid treatment.

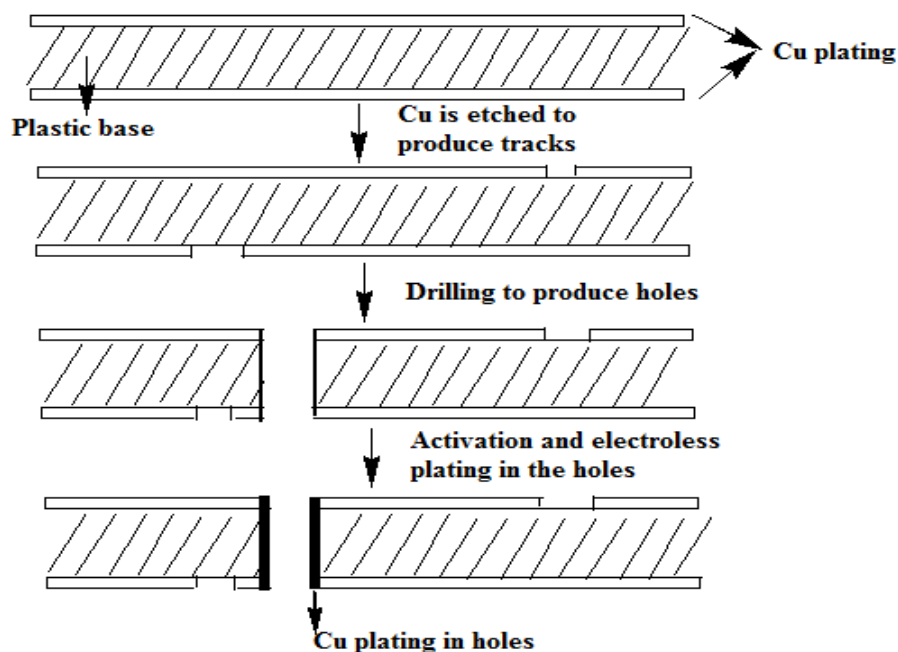
1. Metals like Fe, Co, Ni etc do not need pretreatment.
2. Non-metallic materials (e.g. glass, plastic etc) are activated by first dipping in SnCl<sub>2</sub> and HCl solution, followed by dipping in PdCl<sub>2</sub> solution and dried to get a thin layer of palladium (acts as catalyst).



#### Note:

- Since Cu<sup>2+</sup> ions and HCHO are consumed during the redox reactions, so these are replenished periodically.
- The redox reaction involves the consumption of OH<sup>-</sup> ions, so the pH of the solution decreases, as the reaction progresses. That is why addition of buffer is essential.
- The usual plating rate is 1-5 μm/h.

**Preparation of printed circuit boards (PCB's):** The activated board is immersed in plating bath solution maintained at 25 °C. Plating is carried out at a rate of 1-5 µm/h, till 5-100 µm thickness is obtained. Selected areas are protected by a photo-resist or electroplated image and the rest of the copper is etched away to produce the circuit pattern. The connection between both sides of track is made by drilling hole followed by plating through holes by electro less plating. Double sided PCB's are commonly used because of feasibility of packing of more components in smaller space.



### Distinction Between Electroplating and Electroless Plating:

Property	Electroplating	Electro less plating
Driving force	Direct current	Autocatalytic redox reaction
Reducing agent	Electrons from DC	Electrons from reducing agent
Anode	Separate anode	Catalytic surface of substrate
Cathode	Object to be plated	Object to be plated
Nature of deposit	Not satisfactory for intricate parts with irregular shape and inside of tubes	Satisfactory for all parts
Reactions	At anode: $M \longrightarrow M^{n+} + ne^{-}$ At cathode: $M^{n+} + ne^{-} \longrightarrow M$	Reducing agent + $M^{n+}$ $\rightarrow$ Oxidized product + M
Applicability	Only to conductors	Both conductors and non-conductors