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ENGINEERING CHEMISTRY, 15ECHB102– UNIT 2 - CHAPTER 4: PLATING TECHNIQUES

Introduction

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 technique involves the deposition of a thin layer of a noble metal on a base metal or a polymer or conversion of a thin layer of the surface into the oxide, chromate or phosphate of the metal.

Technological Importance:

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.

1. Provide a bright, shiny appearance.
2. Imparting higher corrosion resistance.
3. High resilience resistance to wear and tear.
4. Providing electrical and thermal conducting surface.
5. To increase abrasion and impact resistance.
6. To increase hardness of the surface.
7. Imparting improved solderability.
8. Providing optical or thermal reflectivity.
9. Imparting chemical and thermal resistance.
10. In the manufacture of metal articles entirely by electroplating.
11. In electroplating and in electrophoretic painting.
12. In electroforming of objects.
13. In electro machining.
14. In electro chemical etching, polishing and engraving.
15. Material restorations.

Two important methods of plating techniques are:

- Electroplating of metals or alloys and

- Electroless plating of metals or alloys

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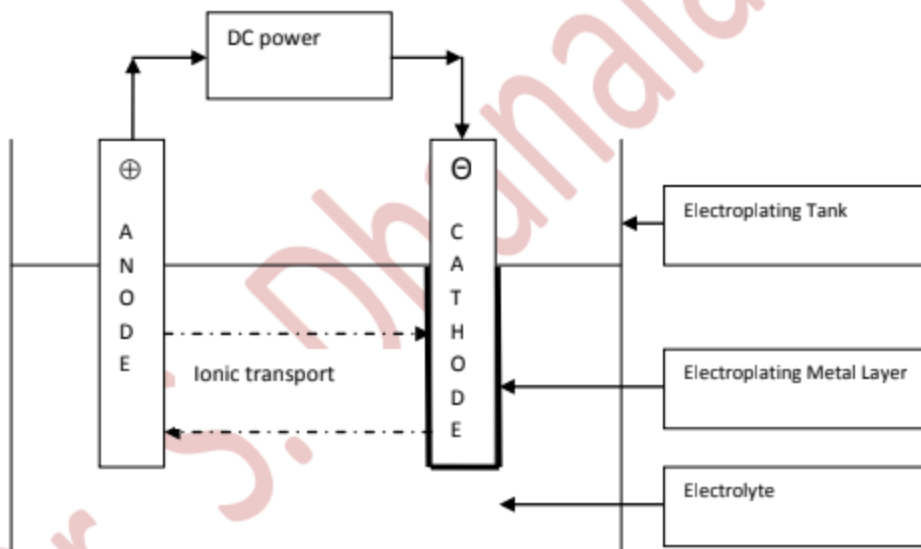## ENGINEERING CHEMISTRY, 15ECHB102– UNIT 2 - CHAPTER 4: PLATING TECHNIQUES

Electro Plating:

The term electroplating refers to the deposition of a metal on the surface of another metal, alloy or any conductor in general, by the process of electrolysis. It consists of a process by which a metal is deposited on another metal or alloy by passing a direct current through an electrolyte solution containing the metal ions to be deposited. Therefore, electroplating can be defined as **"A process in which a base metal is coated with a thin and uniform layer of another suitable metal by electrolytic deposition."**

The common coating metals used are Zn, Cu, Ni, Cr, Ag, Pt, Au, etc., Electro-deposition is an important and frequently used method in industries for producing metal coating.

Electro Plating Process:

The electro-plating device is essentially an electrolytic cell, in which two electrodes, anode and cathode are dipped in an electrolyte solution. The principal components of an electroplating process are shown schematically in the following figure.

Schematic representation of Electro-Plating unit

The essential components include:

1. An electroplating bath containing a conducting salt and the metal to be placed in a soluble form as well as buffer and additives.
2. The electronically conducting cathode, i.e., the article to be plated.
3. The electronically conducting anode, the coating metal itself or an inert material of good electrical conductivity like graphite.
4. An insert vessel to contain the above mentioned materials, made up of either rubber lined steel, plastic, concrete or wood.

Electrolysis Reactions:

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

$$M^{n+} + ne^- \rightarrow M$$

Wherever possible, the preferred anode reaction is the dissolution of the same metal in the solution.

$$M \rightarrow M^{n+} + ne^-$$

In such cases, there is a continuous replenishment of electrolyte during electrolysis.

However, if the anode is made up of an inert material that does not pass into the solution, the electrolytic salt is added continuously in order to maintain optimum metal ion concentration in the solution.

As an example, in the electroplating of copper, the coating metal copper itself is made anode, which dissolves as Cu^{2+} ions, replenishing the Cu^{2+} ions deposited at the cathode.

$CuSO_4$ solution can be used as electrolyte, which ionizes as,

$$Cu\,SO_4 \rightarrow Cu^{2+} + SO_4^{2-}$$

On passing current, Cu^{2+} ions migrate to the cathode and get deposited there.

At the cathode, $Cu^{2+} + 2e^- \rightarrow Cu$

At the anode copper enters into the solution as Cu^{2+} ions.

At the anode, $Cu \rightarrow Cu^{2+} + 2e^-$

Thus in the case, there is a continuous replenishment of electrolyte during electrolysis.

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Characteristics of a Good Deposit:

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

In general, for a given metal, fine grained deposits are smoother, brighter, harder, stronger but less ductile than coarse grained deposits. However, some exceptions do exist.

Requirements of an electrolyte solution for electro plating:

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.

1. Current efficiency (or)
    Cathode efficiency $= \dfrac{\text{weight of metal actually deposited}}{\text{weight of metal calculated from the quantity of electricity passed}} \times 100$

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

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EFFECT OF PLATING VARIABLES ON THE NATRUE OF ELECTRO DEPOSIT

THROWING POWER

The ability of plating bath to give a uniform and even deposit on the entire surface of the object is measured by its throwing power. This is particularly important in object of complex shape. For Ex, Plating in holes and recesses takes place less uniformly than on even surfaces. Throwing power is said to be good if the distribution of the deposit is uniform. This is irrespective of the shape of the object.

Throwing power of plating bath is defined as **"the ability of the bath to produce uniform and even deposit on the entire surface of the substrate".** Experimentally the TP of a plating bath is determined using 'Haring-Blum cell'.
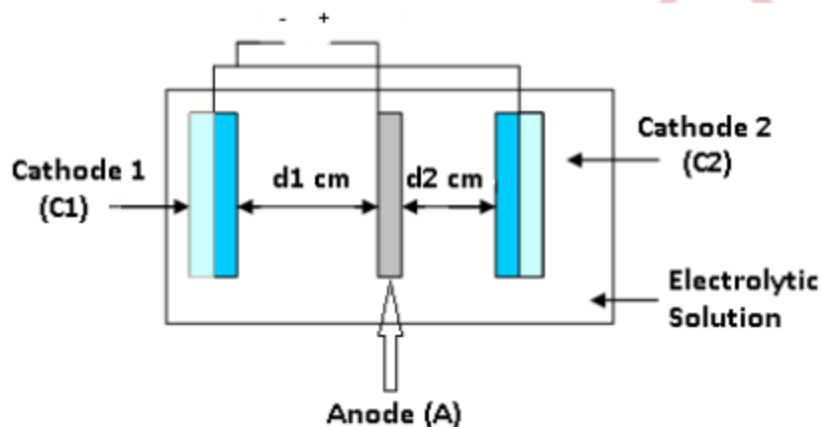
Haring Blum Cell

The **Haring Blum Cell** consists of plating bath solution and an anode (A) at the center of the cell. Two cathodes (C1 & C2) are placed at different distances (d1 & d2 where **d1>d2**) from the anode as shown in the fig.

Article to be plated	Weight of cathodes before deposition	Weight of cathodes after deposition	Weight of metal deposited on cathodes
Cathode 1 (C1)	m1 g	m3 g	W1 = (m3 – m1) g
Cathode 2 (C2)	m2 g	m4 g	W2 = (m4 – m2) g

Initial weights of the cathodes are noted. Electro plating is carried out for a sufficient time and then at the end, the cathodes are weighed again. Finally, the masses W1 and W2 of the metal deposited on the cathodes (C1 & C2) are determined. The mass W1 deposited on the cathode C1 (away from the anode) will be lesser than W2 deposited on cathode C2 (nearer to the anode) i.e., **W1<W2**. The throwing power of the plating bath solution is calculated from the equation

$$\% \text{ Throwing power } = \frac{(X-Y)}{(X+Y-2)} \times 100$$

$$\text{Where, } X = d_1/d_2 \text{ and } Y = W_2/W_1.$$

The throwing power is considered a very good (100%) When W1 = W2, that is the amount deposited is same irrespective of the placement of the electrodes. The throwing power is considered as very poor when its value is -100%.

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.

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Numerical problems on Throwing Power

1. Calculate the percentage of throwing power of plating bath in a Haring Blum cell if the distances between the two cathodes are 6.6 cm and 4 cm from the anode and the masses of the plating on the cathodes are 52 mg and 55 mg respectively.

Solution:

d1 = 6.6 cm; d2 = 4 cm; W1 = 52 mg ; W2 = 55 mg.

X = d1/d2 = 6.6/4 = **1.65**

Y = W2/W1 = 55/52 = **1.0577**

Percentage of Throwing Power = ((X-Y)/(X+Y-2)) * 100

Percentage of TP = {(1.65 – 1.0577) / (1.65 + 1.0577 – 2)} *100

Percentage of Throwing Power = (0.5923 / 0.7077) * 100

✛ **Percentage of Throwing Power = 83.69%**

2. The throwing power of an electrolyte in a Haring Blum cell is 75%. In an experiment, 68 mg of the metal was deposited at the nearest cathode kept at a distance of 4.8 cm from the anode. At what distance must the cathode be kept from the anode if the metal deposited on it was 64 mg?

Solution:

Percentage of Throwing Power, TP = 75%

d_1 =? d_2 = 4.8 cm; W_1 = 64 mg; W_2 = 68 mg

X = d_1/d_2 = $d_1/4.8$.

Therefore, **d_1 = 4.8 * X**

Y = W_2/W_1 = 68/64 = 1.0625.

Percentage of Throwing Power, TP = ((X-Y)/(X+Y-2)) * 100

75 = {(X – 1.0625) / (X + 1.0625 -2)} * 100

75 = {(X – 1.0625) / (X – 0.9375)} * 100

75 * (X – 0.9375) = 100 * (X – 1.0625)

That is, 100 * (X – 1.0625) = 75 * (X – 0.9375)

100 X – 106.25 = 75 X – 70.3125

100 X – 75 X = 106.25 – 70.3125

25 X = 35.9375

Therefore, X = 35.9375 / 25

⬇ **X = 1.4375**

Now, d_1 = 4.8 * X = 4.8 * 1.4375

⬇ **d_1 = 6.9 cm**

3. Calculate the throwing power of a plating bath in a Haring - Blum cell if the distances of the two cathodes from the anode are 6 cm and 5 cm and the quantities of metal deposited are 72 mg and 75 mg respectively. In the same cell if one of the cathode which was fixed at 6 cm was moved to 8 cm from the anode, calculate mass of metal deposited on the electrode.

Solution A:

d_1 = 6 cm; d_2 = 5 cm; W_1 = 72 mg ; W_2 = 75 mg.

X = d_1/d_2 = 6 / 5 = **1.2**

Y = W_2/W_1 = 75 / 72 = **1.042**

Percentage of Throwing Power = ((X-Y)/(X+Y-2)) * 100

Percentage of TP = {(1.2 – 1.042) / (1.2 + 1.042 – 2)} *100

➕ **Percentage of Throwing Power = 65.29%**

Solution B:

Percentage of Throwing Power, TP = 65.29%

d_1 = 8 cm; d_2 = 5 cm; W_1 = ? ; W_2 = 75 mg.

X = d_1/d_2 = 8 / 5 = **1.6**

Y = W_2/W_1 = 75 / W_1

Therefore, **W_1 = 75 / Y**

Percentage of Throwing Power, TP = ((X-Y)/(X+Y-2)) * 100

65.29 = ((1.6 - Y) / (1.6 + Y - 2)) * 100

65.29 = ((1.6 - Y) / (Y – 0.4)) * 100

65.29 * (Y – 0.4) = 100 * (1.6 - Y)

65.29 Y – 26.12 = 160 – 100 Y

That is, 100 Y + 65.29 Y = 160 + 26.12

165.29 Y = 186.12

Therefore, Y = 186.12 / 165.29

➕ **Y = 1.126**

Now, W_1 = 75 / Y = 75 / 1.126

➕ **W_1 = 66.61 mg**

Plating Process

Electroplating of Gold

Gold plating was initially applied for decorative purposes on jewelry articles. But later it is found applications in the industries, for various purposes.

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 70^0C. 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 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 colour 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.

Electroplating of Gold by acid cyanide bath

	Constituents	Bath D (Acidic)
(1)	Plating bath Solutions:	
	(i) Potassium gold cyanide g/dm^3	6.0 – 18.0
	(ii) Mono potassium dihydrogen phosphate g/dm^3	20.0
	(iii) Potassium citrate g/dm^3	50.0
(2)	pH	3 – 6
(3)	Temperature ^{o}C	40 – 70
(4)	Current density (A / ft^2)	1 – 20
(5)	Cathode efficiency (%)	80 – 90
(6)	Brightener	Thiourea
(7)	Leveler	Sodium allyl sulphonate
(8)	Anode	Pt, Platinized Ti, Carbon
(9)	Cathode	Object to be electroplated (It must be free from dirt. Oil and grease, etc., in order to get a good 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. Gold deposit is used for decorative purposes in jewellery, watch cases, pen points, 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.
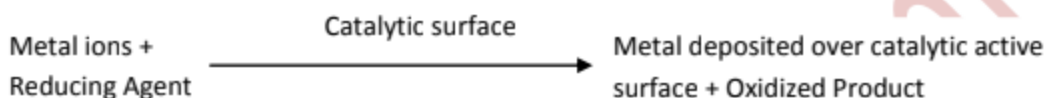
Electroless Plating

Electroless plating 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 electroless plating process can be represented as,

$$\text{Metal ions} + \text{Reducing Agent} \xrightarrow{\text{Catalytic surface}} \text{Metal deposited over catalytic active surface} + \text{Oxidized Product}$$

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**.

The surface to be plated should be catalytically active so that in the beginning of the plating reaction, the surface of the substrate catalyses the reduction. Once the substrate is covered by the metal or alloy coating, the coating catalyses the reduction. The process continues with building of successive layers of metal or alloy.

The catalytic metals such as, Ni, Co, Steel, Fe, Rh, Pd, Al, etc., do not require any surface preparation before electroless plating on them. Non-catalytic metals such as Cu, Brass, Ag, etc., need activation.

This can be achieved by rendering them cathodic for a short period by passing direct current or by dipping in palladium chloride - hydrochloric acid solution. Non conductors like glass, plastics, ceramics, etc., are first activated in a solution of $SnCl_2$ and HCl. After rinsing, it is immersed in a solution of $PdCl_2$ and HCl.

Composition of Electroless Plating bath:

It consists of,

1. Soluble 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. Exaltant or accelerator to increase the rate of plating. Eg., anions like succinate, glycinate & fluoride.
6. Buffer to control pH.
7. Additives like brighteners.

The selection and concentration of complexing agent must be considered very carefully;   because if the metal is too-heavily complexed, sufficient free metal ions will not be available for deposition.

Advantages of Electroless Plating over electroplating:

1. Does not require electrical power source and accessories.

2. Electroless plating is applicable to conductors, semi conductors and insulators like plastics.

3. Throwing power of electroless plating bath is high and hence the objects of irregular shapes can be plated uniformly.

4. Electroless plating are less porous & more compact than electroplating and have a unique chemical, mechanical and magnetic properties.

5. No need of levelers.

6. Electroless deposits are hard.

7. H_2 gas is not trapped.

Electroless plating of copper

Bath Composition

1.	Plating bath	:	12g. / lit. of $CuSO_4$ solution
2.	Reducing Agent	:	8g. / lit. of Formaldehyde
3.	Complexing agent & exaltant	:	20 g. / lit. of EDTA
4.	Buffer	:	14g. / lit. of Rochelle Salt (sodium potassium tartarate) and 12g. / lit. of NaOH
5.	pH	:	11 – 12
6.	Temperature	:	25^oC
7.	Cathode	:	Article to be plated which is catalytically active
8.	Reactions: At Cathode: At Anode: Net Reaction:		$Cu^{2+} + 2e^- \rightarrow Cu$ $2HCHO + 4OH^- \rightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$ $Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2\uparrow$
9.	Plating rate	:	1-5 μm/h
10.	Applications	:	• Widely used for metalizing printed circuit boards • For Producing through – hole connections • For plating on non conductors • As a base for subsequent conventional electro plating • Applied on wave guides and for decorative plating on plastics.

Note:

- Since Cu^{2+} ions and HCHO are consumed during the redox reactions, so these are replenished periodically.
- The redox reaction involves the consumption of OH^- ions, so the pH of the solution decreases, as the reaction progresses. That is why addition of buffer is essential.
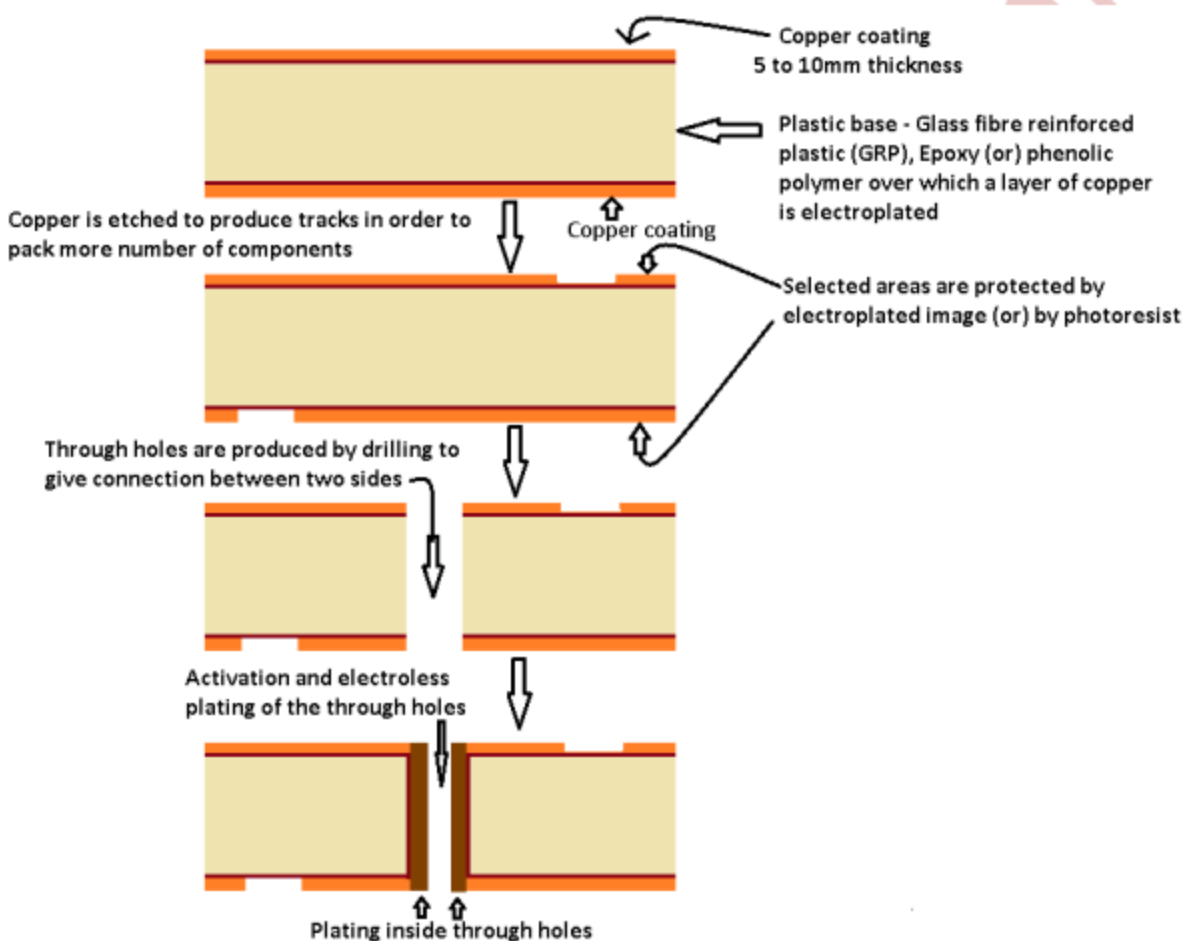
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Preparation of PCB

Through hole connections are necessary when double sided printed circuit boards are fabricated. The electrical connections between two sides of the board are made by drilling hole and then plating through holes by electroless plating.

Steps involved in the manufacture of double sided PCB

Copper coating
5 to 10mm thickness

Plastic base - Glass fibre reinforced plastic (GRP), Epoxy (or) phenolic polymer over which a layer of copper is electroplated

Copper is etched to produce tracks in order to pack more number of components

Copper coating

Selected areas are protected by electroplated image (or) by photoresist

Through holes are produced by drilling to give connection between two sides

Activation and electroless plating of the through holes

Plating inside through holes

For the manufacture of double sided printed circuit boards, the plastic board is initially covered with copper layers by cladding thin layers of electroformed copper foils. i.e., the plating is carried out at room temperature by dipping the activated plastic board in the bath solution.

The temperature is maintained at about $25^{o}C$. The process is continued till a layer of 5 to 10 mm thickness is obtained.   The rate of plating is maintained at 1 to 5 $\mu m\ h^{-1}$.

Selected areas are then protected by a photo-resist or electroplated image and the rest of the copper is etched away to produce the circuit pattern or the track. On etching with suitable etchant the copper except below the printed pattern is etched away, leaving the circuit pattern.

Double-sided copper clad laminates with tracks are preferred because of feasibility of packing of more components in a smaller space.

The connection between two sides is made by drilling hole followed by activation and plating through holes by electroless plating.