Module 4

Surface Finishing (PCB preparation)

Introduction, technological importance of metal finishing. factors affecting the nature of electro deposit - metal ion concentration, current density, complexing agents, organic additives, p^H, temperature & throwing power.

Electroplating – Definition, electroplating process. Methods of cleaning the metal surfaces to be coated. Electroplating of Copper by cyanide bath method and electroplating of gold.

Electroless plating - Definition, distinction between electroplating and electroless plating, advantages of electroless plating. Electroless plating of Nickel and electroless plating of Copper in the manufacture of double-sided PCB.

Corrosion chemistry

Introduction, electrochemical theory of corrosion, types-differential metal, differential aeration (water line and pitting), factors affecting the nature of corrosion.

Corrosion control-galvanization, anodization and sacrificial anode method.

METAL FINISHING (SURFACE FINISHING)

Metal finishing is defined as any process that alters the surface of material for aesthetic or functional purpose

Technological importance of metal finishing:

Metal finishing finds extensive applications in wide variety of industries, The technological importance of metal finishing is in imparting certain additional properties to the materials, in addition to their intrensic properties, includes,

1. Imparting higher corrosion resistance
2. To impart abrasion and wear resistant.
3. To impart hardness.
4. To provide electrical and thermal conducting surface.
5. To impart thermal resistance.
6. To provide optical or thermal reflectivity.
7. To impart improved solderability.
8. In the manufacturing of electrical and electronic components such as PCBs, capacitors, etc.,
9. It is also used in electro polishing and electrochemical etching.

4. ELECTROPLATING

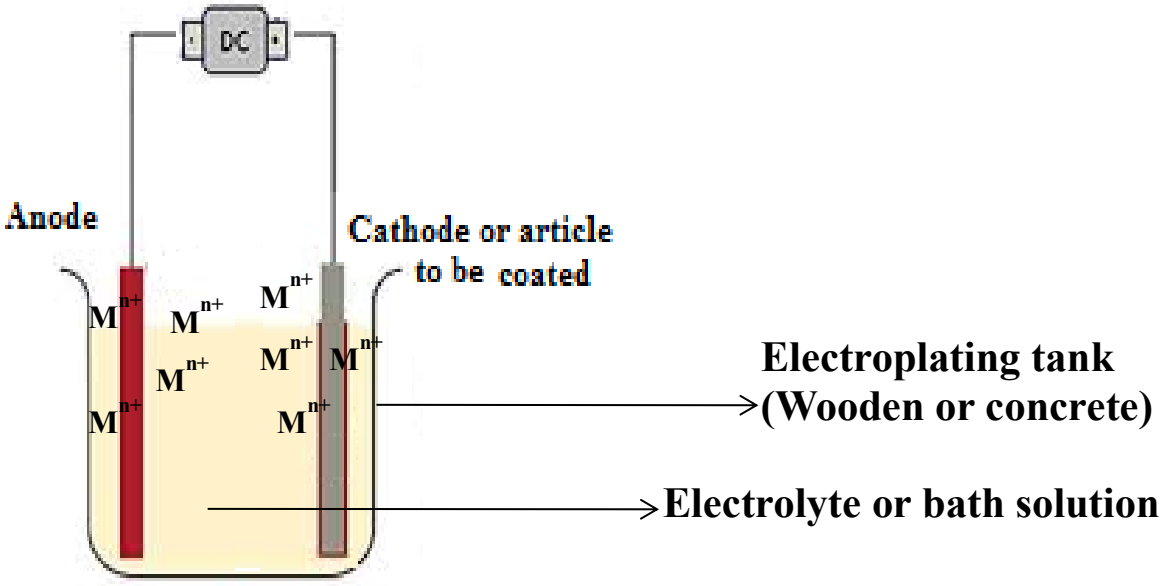
Electroplating is the process of deposition of a metal on to the surface of another metal or alloy by passing a direct current through an electrolytic solution containing the soluble salt of coating metal. The common coating metals used are, Zn, Cu, Ni, Cr, Ag, Au, Pt, etc. The electroplating apparatus consists of the following components.

1) Electroplating bath (electrolytes) containing a conducting salt solution as well as buffer and additives
2) The electrically conducting cathode (the article to be plated).
3) The Electrically conducting anode, the coating metal itself or an inert material of good electrical conducting like graphite
4) An inert vessel to keep the above-mentioned materials, made up of either plastic, concrete or wood

Electrode Reactions:

At Cathode – $M^{n+} + ne^- \rightarrow M$ (Deposition of metal atom at cathode or reduction)

At Anode – $M \rightarrow M^{n+} + ne^-$ (Dissolution of anode or oxidation taken place).



There are many factors which affect the nature of electro deposit, they are,

1) <u>Metal ion concentration and electrolyte</u>

Normally the metal ion concentration is **moderate (about 1-3 moldm^{-3}).** If very **high metal ion** concentration is used, the mass transfer process increases thereby giving **bad quality deposit**. Moderate metal ion concentration results in **good adherent coating films**.

2) <u>Current density</u>

Current density is the current per unit area of the electrode surface. It is expressed in milliampere cm^2 (mAcm^{-2}) or amperes per dm^2. Thickness of metal deposited by electroplating depends up on the current density of the deposited metal. If the **current density is high**, the deposit becomes **loose** as well as **brittle**, therefore **current density should be optimum** and rate for electrodeposition will be extremely low if the current density is low.

3) <u>Complexing agent</u>

By using complexing agent we will able to get fine grained (uniform) and more adherent deposits are obtained.

The complexing agent are used for the following purpose,

a) To prevent the chemical reaction between, cathode metal and plating ions
   Example: During plating of copper on Iron the plating ion Cu^{2+} is complexed with CN^- ions so as to avoid the reaction

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$

b) To avoid the passivation of anodes so that there can dissolve more easily, there by leading to enhanced current efficiency.
c) To improve the throwing power of the plating bath
d) To increase the solubility of the slightly soluble metal salts. (Most commonly used complexing agent are cyanide, hydroxide, sulphate ions etc).

4) Organic additives:

Some organic compounds are added to plating baths to obtain proper coting

a) **Brightener:** Brighteners are used in order to get the **bright** and **lustrous deposit**, the most commonly used brighteners are thiourea, cummarin, aromatic sulphones, sulphonates etc.,
b) **Levelers**: Levelers are used to prevent **uneven deposition**, Sodium allyl sulphate is used as a levelers for nickel deposition.
c) **Structure modifier**: Structure modifiers are used to **decrease internal stress**, internal stress results in micro cracking, and the example of a stress reliever is saccharin.
d) **Wetting agents:** During the electroplating process hydrogen gas is liberated at the cathode. Wetting agents are used to **remove adsorbed H_2** from the cathode surface. They also improve the uniformity of the deposition and reduce brittleness.
An example of a wetting agent is sodium lauryl sulphate.

5) **Temperature:** At low temperatures, electro-deposition may be uniform but slow. At high temperatures deposition may be fast but decomposition of organic additives and corrosion of equipment takes place. Hence, an **optimum temperature** in the range of **35 to 60^0C** is used.
6) **pH**: p^H range should be optimum from 4-8. At low p^H evolution of H_2 gas take place resulting in burnt deposition (bad quality of deposition). At high p^H value precipitation of hydroxides of metal take place on the electrode surface.
Example: Borate buffer for Ni plating pH 4-4.5 and
Citrate buffer for golf plating pH 5-5.5
7) Throwing power: it is the ability of the plating bath to give a uniform coating on the entire surface of the object
If the coating is uniform, then it is said to be good throwing power, the throwing power depends upon
   i. conductivity of the electrolyte
   ii. presence of additives
   iii. complexing agents

Methods of cleaning metal surfaces to be coated.

It is essential to clean the surface of the metal. Common impurities found on the metal surface are oil, grease, an oxide layer (rust) and other matters. The Following methods are employed to clean the metal surfaces.

Solvent cleaning: Solvent cleaning involves the cleaning of the metal surface by using organic solvents such as CCl_4, toluene, xylene, trichloroethylene, etc. these remove the oil and grease-type impurities.

Alkali cleaning: Solvent cleaning removes most of the oil and grease, but minute resides are left behind to remove these residues hot alkali cleaning is used. Na_2CO_3, NaOH, and sodium phosphates are the commonly used alkali cleaners.

Mechanical cleaning: involves the removal of rust and other deposits on a metal surface using a bristle brush and sandpapers.

Pickling: this method is used to remove oxides by dipping in 10% H_2SO_4 or HCl. It also removes traces of alkali.

Electroplating of Copper: (By cyanide bath method)

Plating bath composition	–	40-50 gram CuCN+ 20-30 gram KCN + 10 gram Na_2CO_3 per liter
Operating temperature	–	40-70^{0}C
Current density	–	10-40 mACm^{-2}
pH	–	12-12.6
Additives	–	Sodium thiosulpate or dithiobiurete etc.,
Current efficiency	–	60-90%
Anode	–	High conducting anode
Cathode	–	Article to be plated
Reactions	–	At anode $Cu \rightarrow Cu^{2+} + 2e^-$
		At cathode $Cu^{2+} + 2e^- \rightarrow Cu$
Throwing power	–	Good
Applications	–	In printed circuit boards, as an undercoat for Cr plating and suitable for iron and its alloy plating

Electroplating of gold by acid bath method

Plating bath	Potassium gold cyanide 12-15 g L^{-1}, citric acid 90-115 gL^{-1}, cobalt acetate 0.07-0.1 g L^{-1}
P^H	3.6-4.5
Operating Temperature	40-65 ^0C
Anode	platinized titanium or graphite
Cathode	Article to be coted
Current density	86-252 $mAcm^{-2}$
Current efficiency	70-80%
Additives	Citrate buffer, sodium allyl sulphonate as levelers

Reaction

First step is chemical adsorption step

$$[Au(CN)_2]^- \longrightarrow [Au(CN)]_{(ad)} + CN^-$$

Second step is deposition step

$$[Au(CN)]_{(ad)} + e^- \longrightarrow Au + CN^-$$

Application

- Gold is plated for decorative purposes.
- Gold is plated to improve electrical conductivity.
- Gold is plated to gain thermal stability.

ELECTROLESS PLATING

Electroless plating is a method of depositing a metal from its salt solution on a catalytically active surface (conductor or non-conductor, metal or nonmetal) by a suitable reducing agent without using electrical energy. The added reducing agent causes the reduction of the metallic ions to metal, which gets plated over the catalytically activated surface giving a highly uniform thin coating. The electroless plating process can be represented as,

Catalytic surface

Metal ions + Reducing agent $\rightarrow$ Metal + oxidized product.

The driving force is auto catalytic redox reaction on pretreated catalytic surface.

Active Surface Preparation:

Active surface preparation is most important in electroless plating. This is achieved by using one of the following methods.

i. Etching i.e., by acid treatment

ii. Electroplating a thin layer of the metal to be plated or any other suitable metal. This is usually followed by heat treatment.

iii. Treating with $SnCl_2$ followed by dipping in $PdCl_2$ solution. This treatment gives a thin layer of Pd on the treated surface. Usually, this is followed in the case of plastics, glass, ceramics and PCB's etc.,

COMPOSITION OF ELECTROLESS PLATING BATH

An electroless plating bath in general consists of the following components,

a) Soluble metal salts to provide metal ions for depositions (like chlorides or sulphates)
b) Reducing agents for reduction of metal ions to metal atoms (like formaldehyde, hypo-phosphite, etc.,)
c) complexing agents to complex metal ions to prevent bulk deposition (like citrate, tartarate, succinate, etc.,)
d) Exaltant (accelerator) to increase the rate of plating (like fluoride, glycerate, succinate, etc.,)
e) Stabilizer to give more stability to the solution (like thiourea, cations of lead, calcium, etc.,)
f) Buffer to control pH (like sodium acetate, NaOH and Rochelle salt, etc.,)

Difference between electroplating and electroless plating

Electroplating	**Electroless plating**
Electricity is required	Electricity is not required
Insulators cannot be electroplated	Conductors, semiconductors, and Insulators can be electroless plated
Not have reasonable throwing power	High throwing power
Difficult for plating irregular shape materials	Easily irregular shape materials can be coated
A separate anode is required	Catalytically active surface act as anode
The coating is less hard	The coating is hard

ELECTROLESS PLATING OF NICKEL

Composition of bath per litre:
Coating solution – $NiCl_2$ 20 gram
Reducing agent – Sodium hypo-phosphite 20 gram
Buffer – Sodium acetate 10 gram
Complexing agent– Sodium succinate 15 gram
Optimum pH – 4.5
Optimum temperature - 93^0C
Reactions:

$$Ni^{2+} + 2e^- \rightarrow Ni$$

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^-$$

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+$$

APPLICATIONS

1) Because of their hardness and abrasion resistance, used in industrial components such as pumps and valves, pistons and shafts, parts of hydrolytic system, reaction vessels, tools and dies etc.,
2) Electroless nickel-coated polymers (like ABS plastics, i.e., acrylonitrile – butadiene-styrene) find preferred decorative as well as functional applications.
3) Plastic cabinet coated with Cu and Ni finds applications in digital as well as electronic instruments.

Electroless plating of Copper in the manufacture of double-sided PCB.

Composition of the bath

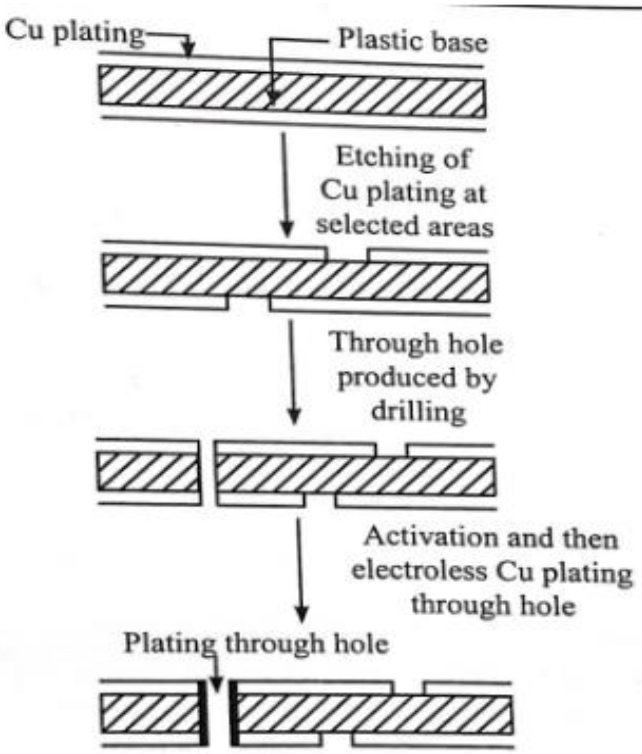
Coating solution	$CuSO_4$ 12g/L
Reducing agent	Formaldehyde 8g/L
Buffer	NaOH 15g/L + Rachelle salt 14g/L
Complexing agent	EDTA 20g/L
p^H	Around 11
Temperature	25 ^{0}C

Reaction

$$2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + 2e^- \quad \text{at anode}$$

$$Cu2^+ + 2e^- \longrightarrow Cu \quad \text{at cathode}$$

$$Cu2^+ + 2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + Cu \quad \text{overal recation}$$



Schematic illustration of electroless copper plating through holes on PCB

- The process involved is known as *subtractive method.*
- A thin layer (5 to 100 μm) of copper is first coated over the PCB (may be glass reinforced/ GR-P/ phenolic/ epoxy polymer).
- The selected areas are protected by employing electroplated image (or photoresist) and the remainder of the plated copper is etched away so as to get required type circuit track.
- More number of components may be packed in a small space by making double sided tracks.
- The connection between the two sides of PCB is provided by drilling holes, followed by electroless Cu plating through holes.

TEXT BOOKS

1. Engineering Chemistry by M.M.Uppal, Khanna Publishers (2001 edition).
2. A text Book of Engineering Chemistry- by P C Jain and Monica Jain, Dhanapatrai Publications, New Delhi.(2015 edition)

REFERENCE BOOKS

1. Principles of Physical Chemistry B.R.Puri, L.R.Sharma & M.S.Pathania, S.Nagin Chand &Co., (2008 edition).
2. Industrial Chemistry by B. K. Sharma, GOEL Publishing House (2014 edition).
3. Industrial Electrochemistry, Second Edition by Derek Pletcher & Frank C. Walsh publisher: Chapman & Hall, USA (1993 edition).