

MODULE 2

Module-II

METAL FINISHING

Metal finishing is the name given to a wide range of processes carried out in order to modify the surface properties of a metal.

The processes involves:

- i) Electroplating of metals, alloys and composites
- ii) Electroless plating of metals, alloys and composites
- iii) Immersion plating of metals (chemical displacement of metals)
- iv) Chemical conversion coatings based on metal compounds (E.g.: Deposition of coatings as oxides, chromates, phosphates, anodizing)
- v) Electrophoretic painting, which involves painting on electrically, charged conducting surface such as motorcar body.

Technological importance of metal finishing:

In early days the primary purpose of metal finishing was to give a decorative appearance to the metal object. In recent times however metal finishing is extended to modify many other surface properties of metals, alloys and composites. The Technological importance of metal finishing is in imparting certain additional properties to the materials in addition to their intrinsic properties so that the utility of the materials is increased.

The technological importance of metal finishing is:

- i. To impart corrosion resistance to metals
- ii. To impart abrasion and wear resistance
- iii. To impart thermal resistance and impact resistance
- iv. To provide electrical and thermal conducting surface
- v. To offer thermal or optical reflectivity
- vi. To impart improved solder ability
- vii. In the manufacture of electrical and electronic components such as printed circuit boards (PCB's), capacitors and contacts
- viii. In electrochemical etching, electrochemical machining and electro polishing

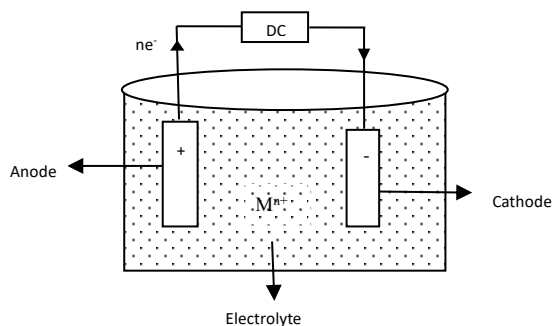
- ix. In electrotyping (to reproduce finely engraved dies or similar finely divided articles such as gramophone records)
- x. To impart hardness
- xi. In electroforming (i.e. to manufacture articles entirely by electroplating)
- xii. To build up material or to restore material
- xiii. To improve the appearance of the articles

Electroplating

Electroplating is a process of deposition of a metal over the surface of a substrate, which may be another metal, alloy or any conductor by electrolysis.

An electroplating 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 include:

- i. An electroplating bath containing an aqueous solution of a soluble salt of the plating metal with a buffer, complexing agent and organic additives.
- ii. The electronically conducting cathode i.e. the article to be plated.
- iii. The electronically conducting anode, may be the plating metal itself or an insoluble inert material, which is a good electronic conductor such as graphite.
- iv. An inert vessel made out of either rubber coated steel, plastic, concrete or wood to contain the above mentioned materials.
- v. A DC power source to carry out electrolysis.



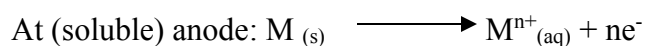
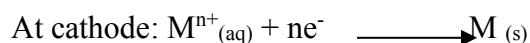
Anode and cathode are dipped in the solution containing the metal ions to be deposited. On passing current, electrolysis occurs and metal at anode dissolves and gets deposited on the object.

During electrolysis, metal ions in the electrolyte solution undergo reduction and get discharged as metal atoms on the cathode surface. Simultaneously some of the oxidizable species present in the electrolyte solution may undergo oxidation at the anode. In such cases, electrolyte is continuously consumed in the electroplating process and is known as **electrolyte consumption method** of electroplating. Therefore electrolyte needs to be replenished periodically to maintain constant electrolyte concentration during electroplating.

But in certain cases the anode can be made of the same metal as it is deposited. In such cases, the anodic metal itself undergoes oxidation at the anode and dissolves in the solution and maintains a constant metal content in the electrolyte. This is known as **anode consumption method** of electroplating.

Electrolysis reactions

During electrolysis the following reactions occur at the electrodes:



In this case metal ions removed at the cathode by reduction are replaced by the oxidation of the anode. If the anode is insoluble and inert, it cannot be oxidized. Therefore as M^{n+} are removed at the cathode by reduction, their concentration in the electrolyte decreases. In order to keep the concentration of the electrolyte at the required level, the electrolytic salt is added to the bath periodically.

Factors governing the electroplating process

The following principles govern electroplating process

a) **Polarization** (b) **Decomposition Voltage or Decomposition Potential** (c) **Over Voltage**

(a) Polarization

Polarization is defined as a process where there is a variation of electrode potential due to inadequate supply of ions to the electrode from the bulk of the solution.

The diffusion of M^{n+} ions to the cathode is slower than they are reduced, there would be a delay in the establishment of equilibrium between the metal and its ions at the cathode. This results in the polarization of the electrode. Therefore excess voltage over the theoretical voltage is required to carryout

electroplating. Therefore, a cell that requires excess voltage over the theoretical is said to be polarized and the phenomenon is referred to as polarization.

➤ The observed polarisation is

(a) due to the variation in concentration of the ions around an electrode (concentration polarization) and

(b) due to the accumulation of products around an electrode, where the products discharged at the electrodes during electrolysis set up additional active electrodes whose potential (back emf) oppose the applied potential.

➤ Polarization of the electrode depends on the:

- i. Nature of the electrode - Size, shape and composition of the electrode
- ii. Concentration of the electrolyte and its conductivity
- iii. Temperature
- iv. Products formed at the electrodes
- v. Rate of stirring
- vi.

➤ Concentration polarization can be minimized by using

- i. Large electrode surface
- ii. Low concentration of the electrolyte
- iii. Electrolyte with high ionic conduction
- iv. Continuous stirring to ensure rapid ionic diffusion to electrodes and minimize a concentration gradient
- v. Increasing temperature

(b) **Decomposition potential or Decomposition voltage:**

The decomposition potential or voltage is defined as the minimum external voltage that has to be applied between the electrodes to bring about continuous electrolysis of an electrolyte.

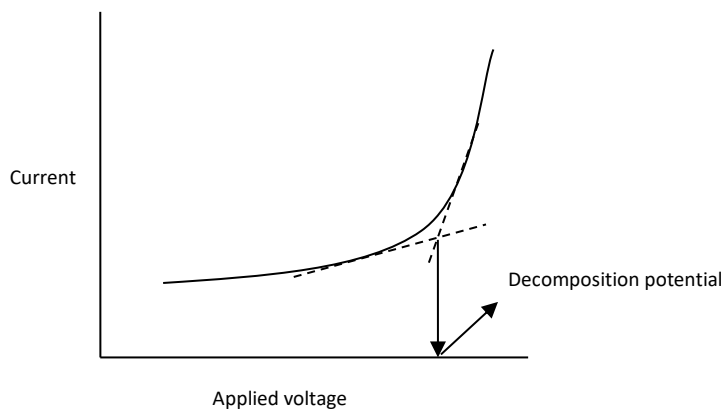
The actual decomposition potential required is much higher than the theoretically calculated decomposition potential. Below the decomposition voltage no continuous electrolysis occurs due to the products liberated at the electrodes. This is because

- i. The products liberated prevent the diffusion of the ions to the surface of the electrodes setting up polarization. And due to **polarization** more voltage becomes necessary to carryout electrolysis.
- ii. The products liberated at the electrodes also forms the secondary cell producing back emf which opposes applied emf and nullifies applied potential and continuous electrolysis doesn't occur.

For Example: In the electrolysis of water, Continuous electrolysis occurs only when the applied emf is sufficient enough to overcome the back emf. Experimentally it is determined that decomposition potential of water is 1.7 V below which continuous electrolysis doesn't occur.

The external voltage applied using battery E to the electrolyte in the cell is altered using the variable resistance C. The applied voltage is measured using the voltmeter V. Using the milli ammeter A the current passing through the electrolyte is measured for every change in the applied voltage. A series of readings of current verses applied voltage are recorded starting from very low voltage to high voltage resulting in continuous electrolysis.

The current is plotted against the applied voltage. The curves are extrapolated. Their point of intersection gives the decomposition potential. From the graph it is clear that if voltage is increased above decomposition potential then current also increases.. Below the decomposition potential the increase in current is only marginal indicating that no electrolysis is taking place.



➤ **Significance of decomposition potential**

- i. Knowledge of the decomposition potentials of an electrolyte is helpful in choosing the right voltage required for the continuous electrolysis of the electrolyte.
- ii. Different electrolytes have different decomposition potential. Therefore knowledge of their decomposition potential is helpful in predicting the order in which various metals will be discharged from a mixture of their electrolytes. The easily discharged ions get discharged first. For example: If a mixture of equimolar quantities of CuSO_4 , ZnSO_4 and CdSO_4 is electrolyzed, because of the difference in their decomposition potentials, we get copper discharged first followed by Cadmium and finally Zinc is discharged at the cathode.

(c) **Over Voltage:**

Over voltage is the excess voltage that has to be applied above the theoretical discharge potential (reversible electrode potential) to bring about the continuous electrolysis.

Over voltage = Actual decomposition potential – Theoretical discharge potential.

For most metals, the discharge potentials are almost equal to or slightly higher than their reversible electrode potentials in a given solution of their ions. But in the case of gases like H_2 and O_2 , the discharge potentials are appreciably higher than their reversible electrode potentials. The excess voltage required above the reversible electrode potential is called over-voltage.

For example during the electrolysis of water, under standard conditions the discharge potential of gas on smooth platinum electrode should be 1.3 Volt. However the actual evolution of the gas at the platinum electrode occurs at 1.7 Volt. The extra 0.4 Volt required above the theoretical discharge potential is called over-voltage on smooth platinum surface.

$$\begin{aligned}\text{Over voltage} &= \text{Actual discharge potential} - \text{theoretical discharge potential} \\ &= 1.7 - 1.3 = 0.4 \text{ Volt}\end{aligned}$$

Over-voltage is believed to be a surface phenomenon at the electrodes. The evolution of a gas involves several steps. At least one of the steps is a slow process requiring extra energy to take place this is supplied by the overvoltage.

- The following factors influence the overvoltage:
- (i) Electrode surface
 - (ii) Nature of the electrolyte

- (iii) Nature of the substance discharged
- (iv) Current density
- (v) Temperature

The over voltage of the same gas on different metal surfaces will be different. **Hydrogen over voltage** is the excess voltage required to liberate hydrogen on an electrode. More hydrogen over voltage less easier is the liberation of hydrogen on the electrode.

Electroplating of Chromium:

Metal objects to be chrome plated are first given an undercoat of nickel so that only a thin chromium plating is required. The nickel undercoat gives corrosion protection. On ferrous metals an undercoat of copper followed by nickel is applied before plating.

Sl.No.	Bath Condition	For Decorative Plating	For Hard Chrome Plating (Industrial or Engineering chromium)
1.	Bath composition	250g of chromic acid (H_2CrO_4) + 2.5g of conc. H_2SO_4 + 1g of trivalent chromium (Cr^{3+}) per litre of the bath (Ratio between H_2CrO_4 and H_2SO_4 is 100:1).	250g of chromic acid (H_2CrO_4) + 2.5g of conc. H_2SO_4 + 1g of trivalent chromium (Cr^{3+}) per litre of the bath
2.	Temperature $^{\circ}\text{C}$	45 - 55 $^{\circ}\text{C}$	45 - 55 $^{\circ}\text{C}$
3.	Current density	145 – 430 A/ ft^2	290-580 A/ ft^2
4.	Anode	Insoluble anodes like Pb-Sb, Pb-Sn, graphite	Insoluble anodes like Pb-Sb, Pb-Sn, graphite
5.	Cathode	Article to be plated	Article to be plated
6.	Thickness	0.25-0.75 μm	2.5-300 μm

Anode and cathode are suspended in the electrolytic bath and electrolysis is carried out using a DC source. On electrolysis, chromium plate will be formed on the object at the cathode.

Cathode reaction: $\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$

The Chromium plating bath contains chromic acid, where chromium is in +6 Oxidation state. Sulphate ions from H_2SO_4 act as catalyst and bring about the conversion of Cr (VI) to Cr (III) at the anode by a complex reaction. Cr^{3+} ions formed are discharged at the cathode to give the chromium plating.

To obtain a good and attractive chrome plating the concentration of Cr^{3+} should be low. In chrome plating insoluble anodes are used instead of soluble chromium anodes. This is because when chromium anodes are used the anode efficiency is five times more than the cathode efficiency that is chromium anode goes into solution as Cr^{3+} ions five times faster than these ions are discharged at the cathode as chromium plate. This builds up the Cr^{3+} ions in the bath; which leads to an imbalance in bath composition with respect to Cr (III) – Cr (VI) ratio and chromic acid - H_2SO_4 ratio, both of which are important factors in deciding the nature of the deposit. A large concentration Cr^{3+} ions in the bath leads to a black chromium deposit on the cathode.

There is also a possibility of chromium metal passivating in acid sulphate medium.

Applications of Decorative chrome plating:

Decorative chromium plating produces an attractive coating resistant to corrosion, and wear and abrasion. It is applied to:

- i) Bicycle handles and tyre-rims, motorcar bumpers and head light holders, aircraft parts, steel furniture and decorative articles.
- ii) Bathroom fittings like taps, showers and shower cords, handrails etc.
- iii) Dental and surgical instruments.

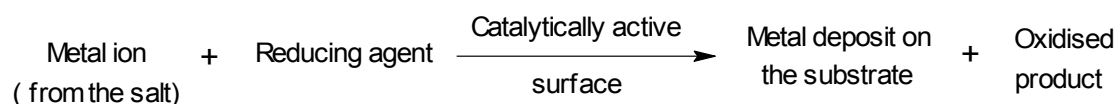
Applications of Hard chrome plating:

- i) Hard chrome plating is applied to several components of machinery used in industries, like for dies, cutting tools, piston rings, cylinder liners, crank shafts of marine and aeroengines, bearings, hydraulic rams etc.
- ii) Hard chrome plating is used to build up worn out and mismatched parts.
- iii) Black chrome plating is used in optical instruments, machine tools and electronic parts.
- iv) Used as a coating for solar energy collectors.

Electroless plating:

Electroless plating is a process of depositing a metal or an alloy on a catalytically active surface of a substrate by chemical reduction of the metal ions using a suitable reducing agent, without the use of electrical energy.

The substrate may be a conductor like a metal or an alloy or a non-conductor like glass, plastic, ceramic etc. Metal ions get reduced by the reducing agent to metal, which plates over the catalytically active surface of the substrate.



The surface to be plated should be catalytically active so that in the beginning of the plating reaction atoms of the substrate catalyze the reduction of the metal ions to the metal. Once a layer of metal atoms is deposited on the surface of the substrate, they catalyze further reduction of the metal ions. The reduction process continues building up of successive layers of the metal. Therefore electroless plating is also called as autocatalytic plating.

Advantages of Electroless plating over Electroplating: -

1. There is no need for electrical power and therefore the problems of polarization, over voltage etc do not arise.
2. Conductors like metals and alloys, semiconductors and also non-conductors like glass, plastics and ceramics can be electro less plated. (Non conductors cannot be electroplated.)
3. Electroless baths have excellent throwing power. Objects with irregular shapes, with recesses or holes can be uniformly coated.
4. Electroless coatings are harder than those produced by electroplating and therefore exhibit good abrasion resistance.
5. The electroless coatings obtained are less porous with unique chemical, mechanical and magnetic properties.

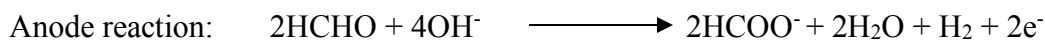
Distinction between Electroplating and Electroless plating

Sl.No	Property	Electroplating	Electroless plating
1.	Driving force	Power supply	Autocatalytic redox reaction
2.	Site of the cathode reaction	Article to be plated.	Article to be plated with a catalytically active surface.
3.	Nature of the cathode	Has to be an electronic conductor like a metal or an alloy.	Need not be an electronic conductor. Non-conductors like glass, plastics etc and semiconductors can be plated in addition to metallic conductors.
4.	Cathode reaction	$M^{n+} + ne^- \longrightarrow M_{(s)}$	$M^{n+} + ne^- \longrightarrow M_{(s)}$
5.	Site of anode reaction	Separate anode is required.	Separate anode is not required. The article to be plated is the site of anode reaction.
6.	Anode reactant	M or H ₂ O	Reducing agent, R
7.	Anode reaction	Oxidation of the soluble metal anode to give ions. $M_{(s)} \longrightarrow M^{n+} + ne^-$ Or Oxidation of water to oxygen at the inert anode. $n/2H_2O \longrightarrow n/4O_2 + nH^+ + ne^-$	Oxidation of the reducing agent on the catalytically active surface of the article plated. $R \longrightarrow \text{oxidized product} + ne^-$
8.	Nature of deposit	Pure metal or definite alloy	Metal contaminated with oxidized / reducing species
9.	Thickness limit(μm)	1-100	1-100
10.	Cause of reduction	Electrical energy	Reducing agent

Electroless plating of copper

The surface to be plated is cleaned to free of impurities and activated if required. The activated surface is dipped in the following electroless plating bath solution.

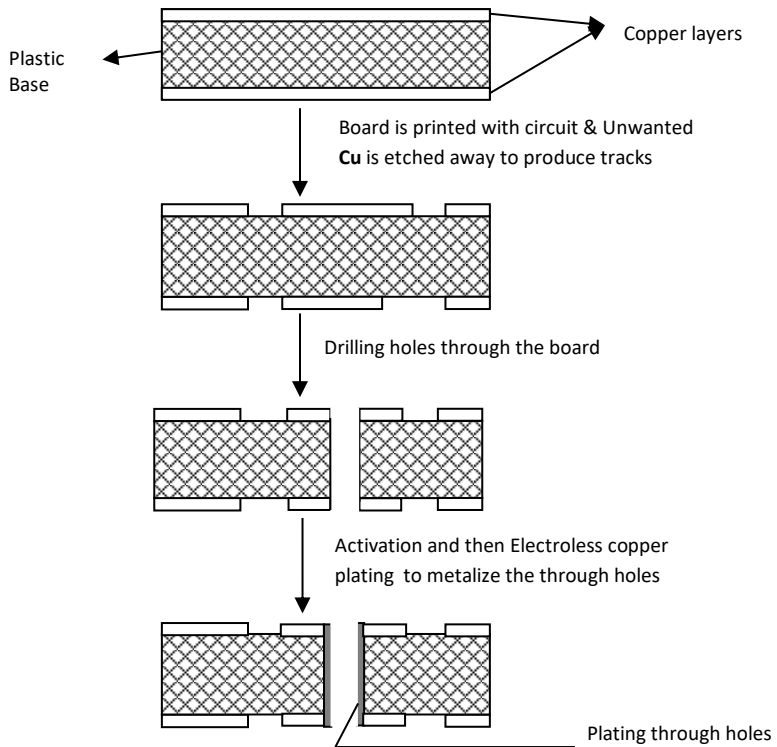
1.	Electroactive metal salt solution	CuSO ₄ - 12g per litre
2.	Reducing agent	HCHO - 8g per litre
3.	Buffer	14g of Rochelle salt + 15g of NaOH per litre
4.	Complexing agent and exaltant	EDTA- 20g per litre
5.	pH	11
6.	Temperature	25 ⁰ C



Manufacture of double sided Printed Circuit Board (PCB) with copper

(First write bath composition and reactions involved in Electroless plating of copper)

In the manufacture of double sided PCB, the plastic board is initially covered with copper layers by cladding thin layers of electro formed copper foils. Then both sides of the copper clad board are printed with etch-resistant circuit patterns or the tracking is given on both sides. Later on etching with suitable etchant, the copper except below the printed pattern is etched away, leaving the circuit pattern. Electrical connection between the two side circuits are made by drilling a hole through the board. The hole is then activated and electroless plated with copper, as it cannot be electroplated.



Electroless plating of Nickel

The metallic surface is first degreased using organic solvents or by alkali treatment followed by pickling. Al, Fe, Cu and brass need no activation. Stainless steel is activated by dipping in 1:1 H₂SO₄. Magnesium alloys are given a zinc or copper undercoat by electroplating. Insulators like Plastics, glass and quartz are activated by dipping in SnCl₂ containing HCl and then in PdCl₂.

Bath Composition:

A solution of NiCl₂(20g/l)

Sodium hypophosphite(20g/l)- reducing agent

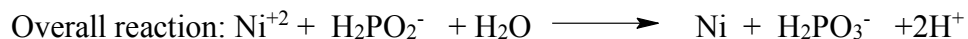
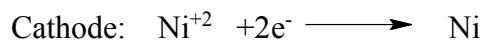
Sodium acetate(10g/l) – buffer

Sodium succinate(15g/l)- complexing agent and exaltant

pH - 4-5

Temp- 73-93°C

Reactions



During the reaction H⁺ ions are released and pH decreases. This affects the quality of plating. The buffer controls the pH during plating.

