

Metal finishing is a surface process carried out in order to modify the surface properties of a metal by deposition of a layer of another metal or an alloy or a polymer film.

Egs: electroplating of metals, electroless plating, chemical conversion coating etc.

Technological importance of metal finishing:

Metal finishing imparts desirable surface characteristics such as

1. Imparting higher corrosion resistance.
2. Imparting improved wear resistance.
3. Imparting thermal resistance, hardness, improved solderability etc.
4. Providing optical or thermal conducting surface.
5. Manufacturing electrical and electronic components such as PCB, capacitors etc.
6. Electroforming of articles.
7. In electro polishing and electrochemical etching.

Electroplating

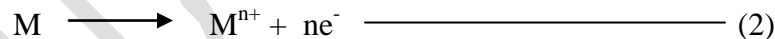
It is a process of depositing a metal or an alloy or a composite on to a surface by means of electrolysis.

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.

During electroplating the object to be plated is made as cathode in an electrolytic bath containing metal ion to be plated. The reaction occurring at the cathode is



The possible anodic reaction is the dissolution of the same metal



The electrolysis conditions are controlled in such a way that current efficiency of reaction 1 and 2 are the same hence the concentration of M^{n+} in the bath solution remains constant during electroplating. In some cases inert anodes such as PbO_2 , stainless steel, pt, carbon etc. are used. In such cases metal salts are added frequently to maintain the M^{n+} concentration. At cathode and anode other reaction other than metal deposition and dissociation are, H_2 evolution at cathode and O_2 evolution at anode. For successful electroplating process, correct pretreatment of the surface, proper plating bath composition, current density, temperature, selection of anodes and other plating conditions are necessary.

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

1. Current density: current density is the applied current per unit area of the cathode surface. It is usually expressed in milliamperes/cm² or amp/dm².

The quality of the electrodeposit depends on the current density used in electroplating. As the applied potential increases current density increases and attains a limiting value.

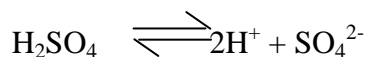
- i. *At low current density:* deposit obtained will be large grain and loosely held at the cathode surface because surface diffusion process is faster than the electron transfer.
- ii. *At moderate current density:* Electroplating at the moderate current density, below limiting value results in fine grain and uniform deposits.
- iii. *At high current density:* deposits are non-compact, rough and powdery because mass transport in solution by diffusion of ions to the electrode surface predominates. At very high current density above the limiting value electrodeposit obtained will be irregular, spongy, discontinuous, loosely held and said to be burnt practical demand. This is because the evolution of hydrogen on the surface of the electrode predominates, thereby causing faster depletion of H⁺ ions in the vicinity of the cathode.

Therefore **moderate** current density well below the limiting value should be applied for plating to obtain desired quality of electrodeposit.

2. Metal salt concentration and electrolyte concentration: Metal ions always are added in high concentration to avoid rapid depletion in the vicinity of the cathode during electroplating. More soluble metal salts are used. High current density can be employed at high metal salt concentration.

Electrolytes are also added in high concentration to increase the conductivity of the plating bath solution and cathode efficiency. And also the added electrolyte sometimes acts as a buffer solution.

3. Metal ion concentration: Low metal ions concentration decreases the crystal size and results in fine adhering coating film. Low concentration of metal ion can be achieved by either by addition of a compound with a common ion or by formation of complex compounds.



4. Complexing agents: Complexing agents are added

1. To maintain low metal ion concentration in solution.

2. To avoid the reaction between cathode metal and plating metal 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.

6.Organic additives: wide ranges of organic compounds are added in relatively low concentration to modify the structure, morphology and properties of the deposits.

Addition agents are classified into several groups based on their type of action.

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. They usually cause the formation of even fine-grained deposits by modification of nucleation process.

Usually used brighteners are aromatic sulphones or sulphonates and thiourea, coumarin etc.

Levellers: These compounds produce a leveled deposit on a more macroscopic scale and act by adsorption at points where there would be rapid deposition of metal. 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.

Egs: Sodium alkyl sulphonate. Sometimes brighteners also acts as levelers.

Stress reliever [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. These types of additives are called as stress relievers.

Saccharin is used as stress reliever in nickel plating.

Wetting agents: During electroplating in some cases there is simultaneous deposition of hydrogen and metal at the cathode. If bubbles of hydrogen adhere to the cathode surface strongly, plating is prevented around the bubble and a pit is created in the coating. The hydrogen occluded in the deposit results in hydrogen embrittlement. Some surface- active agents are added to detach adsorbed hydrogen and eliminate pitting.

Egs: Sodium lauryl sulphate is used as wetting agent in plating bath of Ni and Zn.

6. **pH:** For a good electrodeposit, the P^H of the bath must be properly maintained. At low pH since hydrogen ion concentration will be more hence, evolution of hydrogen at cathode occurs, resulting in a spongy deposit.

At high pH hydroxides are formed at the cathode and resulting burnt deposit. Hence optimum pH range for most plating baths should be from 4 to 8.

7. **Temperature:** A good fine grain and smooth deposit is obtained at slightly higher temperature because at high temperature solubility and dissociation of metal salt increases, which in turn leads to a higher conductivity of the solution. But the disadvantages of maintaining the higher temperature are, corrosion of process equipment, hydrogen evolution at the cathode and decomposition of organic addition agents may take place. Hence **moderate** temperature is maintained.

Throwing power of the plating bath: “The ability of a plating bath solution to give an even and uniform deposit on the entire surface of cathode of irregular shape is called throwing power.”

Throwing power of plating bath can be determined by using the haring-blum cell.

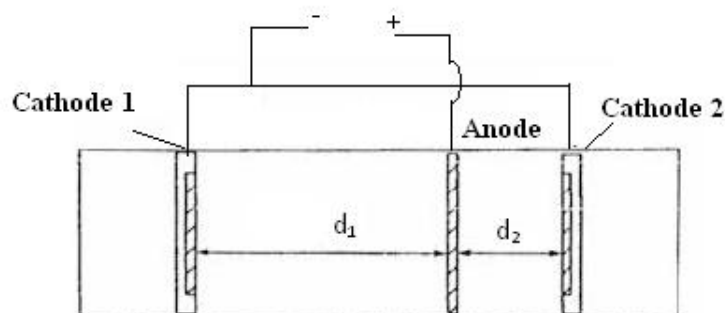
The cell contains plating bath solution whose throwing power is to be determined. The two cathodes are placed at different distances d_1 and d_2 where $d_1 > d_2$ from a single central anode and electroplating is carried out.

The weight of the metal plated on the two cathodes W_1 and W_2 are determined. W_1 is for d_1 and W_2 is for d_2 .

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

where $K = d_1 / d_2$, $M = W_2 / W_1$

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%).

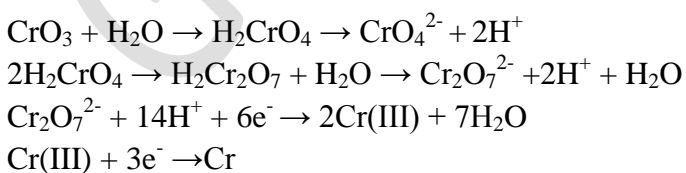


Haring-Blum Cell

Electroplating of chromium:

Chromium plating	Decorative Chrome plating	Hard Chrome plating
Anode:	Insoluble anodes like Pb-Sn, Pb-Sb or stainless steel coated with PbO ₂	Insoluble anodes like Pb-Sn, Pb-Sb coated with PbO ₂
Cathode:	Object to be plated	Object to be plated
Bath Composition	Chromic acid and sulphuric acid in the ratio 100:1	Chromic acid and sulphuric acid in the ratio 100:1
Current density (mA cm ⁻²)	100-200	215-430
Temperature	45-60 °C	45-60 °C
Current Efficiency (%)	8 – 12	10 -15
Applications	Provides durable and good decorative finish on automobiles, surgical instruments etc.	Extensively used in Industrial and engineering applications

Plating bath contains chromium trioxide (chromic acid), during electroplating of chromium Cr(VI) is reduced Cr(III) in the presence of SO₄²⁻ catalyst (furnished by sulphuric acid). Cr(III) is reduced to Cr (0) which gets deposited on the substrate



Why Chromium anode is not used in Cr plating?

Chromium anode is never used in Cr plating due to the fact that Cr metal passivates strongly in acid medium. Moreover, Cr anode on dissolution gives rise to Cr(III) ions which lead to the formation of black deposit.

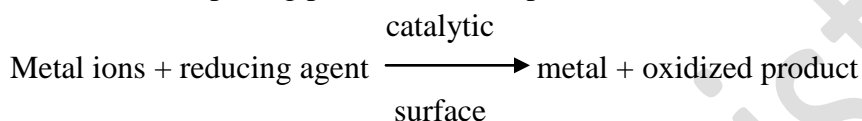
Note: PbO₂ coating on anode oxidizes Cr (III) to Cr (VI) and thus controls the concentration of Cr (III) ions. In presence of large quantity of Cr (III) ions a black deposit is obtained.

Electro less plating

Electro less 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 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.

Metals such as Ni, Co, steel, Fe, Rh, Pd, Al etc. do not require any surface preparation but non-catalytic metal such as Cu, Brass, Ag etc need activation. This can be done 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 SnCl₂ and HCl. After rinsing it is immersed in a solution of PdCl₂ and HCl.

Comparison of electro less and electroplating:

Property	electroplating	electro less plating
Driving force	Power supply	Autocatalytic redox reaction
Cathodic reaction	$M^{n+} + ne^- \longrightarrow M$	$M^{n+} + ne^- \longrightarrow M$
Anodic reaction	$M \longrightarrow M^{n+} + ne^-$ or $n/2 H_2O \longrightarrow n/4 O_2 + nH^+ + ne^-$	$R \longrightarrow O + ne^-$
Site of cathodic reaction	article to be plated	article to be plated (catalytic surface)
Site of anodic react:	separate anode	article to be plated
Anode reactant	M or H ₂ O	reducing agent.
Nature of deposit	pure metal or definite alloy	metal with reducing agent & oxidized products as impurities

Electroless plating of copper:

Pretreatment and activation of the surface: 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, plastics, printed circuit boards, PCB) are activated by first dipping in SnCl_2 and HCl solution, followed by dipping in PdCl_2 solution and dried.

Composition of bath:

Coating solution: CuSO_4 solution (12g/L)

Reducing agent: Formaldehyde (8g/L)

Buffer: NaOH (15g/L) + Rochelle salt (14g/L)

Complexing agent: EDTA (20g/L)

pH: 11.0

Temperature: 25°C

Reactions:



Applications:

1. Mainly used in printed circuit boards (PCB).
2. For plating on non-conductors.
3. Applied on wave-guides and for decorative plating on plastics.

Preparation of printed circuit boards (PCB): A PCB is made of glass-reinforced rubber like GR-P or epoxy or phenolic polymer. A thin layer of copper is electroplated over the PCB. Then, selected areas are protected by employing electroplated image and the remaining part of the plated copper is removed by etching 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.

