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Metal Finishing

Introduction:

Metals such as gold and silver are used in ornaments, aluminium and copper and their alloys and stainless steel in household articles and steel in manufacture of machines and machinery Parts. None of these Metal posses and properties such as :

- Resistance to corrosion
- Resistance to wear and tear
- Resistance to Impact etc.

These properties are required for their use in variety of engineering applications. In order to satisfy the conditions of their applications we need a process called Metal Finishing.

"Metal finishing is defined as the process involving the deposition of thin layer of suitable metal over base metal or conversion of thin layer of the surface into its metal oxide".

Most widely used metal finishing techniques are Electroplating and Electro less plating.

The primary importance of metal finishing is to give decorative appearance to objects. But there is number of other important applications of metal finishing which includes:

1. To provide resistance to corrosion 2. To provide resistance to wear and tear
3. To provide resistance to impact 4. To provide electrical and thermal conducting surface.
5. To provide bright and shiny surface 6. To impart thermal and electrical conductivity
7. To increase the hardness of the surface 8. To provide chemical resistance
9. To provide optical reflectivity

This technique is also used in the manufacturing of electronic and electrical components such as printed circuit boards, capacitors, contact points and also used in electroforming, electro polishing, electrochemical etching.

Theory of electroplating:

The process of depositing thin and uniform layer of suitable metal over the surface of another metal by the process of electrolysis is called as electroplating.

Since the process of electroplating involves electrolysis it is very important to understand the concept of faraday"s laws of electrolysis.

When an electric current is passed through electrolyte solution, cations move towards cathode where they get reduced where as anions move towards anode where they get oxidized. This decomposition of an electrolyte by passing an electric current is called electrolysis.

In electroplating, object to be coated is taken as cathode and is connected to negative terminal. Whereas anode is connected to positive terminal of the battery.

When an electric current is passed through the solution, oxidation takes place at the surface of anode and metal ions present in the solution is reduced to metal atoms and get deposited over the surface of cathode (object).

$$M \rightarrow M^{n+} + ne^{-} \text{ (At Anode)}$$

$$M^{n+} + ne^{-} \rightarrow M \text{ (At Cathode)}$$

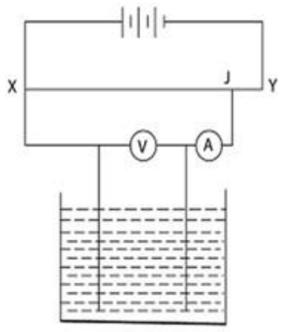
The amount of substance oxidized at anode are reduced at cathode depends on the quantity of electric current passed through solution. This reaction is explained by faraday's law of electrolysis.

Electro plating involves electrolysis. This electrolysis involves the important electrochemical principles which are very important for successful deposition of the metal. Or **The fundamental principles governing metal finishing are,**

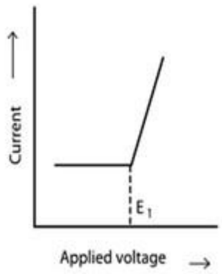
- Decomposition Potential(E_D)
- Over potential or Over voltage(η)
- Polarization of the electrode

Decomposition potential: it is defined as the minimum external potential required of the continuous electrolysis of the electrolyte.

Experimental Determination of Decomposition Potential:



Electrolytic Cell



Decomposition Potential

The electrolytic cell consists of two platinum electrodes immersed in an electrolyte solution whose decomposition potential is to be measured. The electrodes are connected to a volt meter V, an ammeter A, and movable jockey J in series.

The voltage is varied by moving jockey "j" along the wire XY and the corresponding current is measured using ammeter. Up to a definite potential, the current flow is very small and there after increases with increase in potential.

Plot a graph of current verses applied voltage as shown in figure b. the intersection of the two straight line portions of the graph gives the decomposition potential E_D.

Over potential or Over voltage (η):

In most of the cases, experimental decomposition potential (E_D) required to carry out continuous electrolysis is greater than theoretical decomposition potential. This difference in potential between practical decomposition potential and theoretical decomposition potential is called as over potential (η).

Over potential (η)=Experimental decomposition potential –Theoretical decomposition potential.

$$\eta = E_D - E_{back}$$

Therefore, over potential is defined as the excess potential that has to be applied over and above the theoretical decomposition potential of an electrolyte to start electrolysis.

Over potential depends on several factors:

1. Nature and physical state of the metal electrodes 2. Current density applied
3. Nature of the material deposited. 4. Temperature.
5. Rate of stirring of the electrolyte solution. 6. Nature of the electrolyte.

Polarisation of an Electrode:

If M^{n+} is the concentration of metal ions surrounding the electrode solutions interface at equilibrium.

When a direct current is passed through the electrode solution interface, the metal ion concentration at the vicinity of the electrode surface decreases owing to the reduction of metal ions to metal atoms.

Therefore, there is a shift in the equilibrium and a change in electrode potential.

This can explained on the basis of Nernst Equation we know that,

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

As the metal ion concentration decreases electrode potential at the surface of the electrode decreases.Therefore, electrode is set to be polarised.

Therefore, "Polarisation is defined as a process in which there is a variation in electrode potential due to slow supply of metal ions from the bulk of solution to the surface of the electrode".

Polarisation of electrodes depends on several factors like,

1. Nature of the Electrode (Size, Shape, Composition) 2. Concentration Of electrolyte and its conductivity
3. Temperature 4. Rate of stirring of the electrolyte

Effect of polarisation can be minimised by stirring the electrolyte continuously and by using electrodes of larger surface area and electrolytes of higher Conductivity.

Characteristics of a good deposit:

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

Electroplating of chromium: This chromium plating is carried to give decorative coating to the surface and to give hard coating. The main aspect of the 2 process is same except that for hard chromium plating higher current density is applied. The special features of electroplating bath are given below.

Particulars	Decorative	Hard
Bath composition	250 g chromic acid + 2.5 g Con. H_2SO_4/dm^3	200 g chromic acid + 2.5 g Con. H_2SO_4/dm^3
Current density	20-40 mA/cm^2	30-60 mA/cm^2
Temperature	313-328 K	313-328 K
Anode	Insoluble Pb-Sn alloy with PbO2 coating	Insoluble Pb-Sn alloy with PbO2 coating
Cathode	Object to be coated	Object to be coated

Reactions:

$$CrO_3 + H_2O \rightarrow H_2CrO_4$$
$$H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O$$
$$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \xrightarrow{SO_4^{2-}} 2Cr^{3+} + 7H_2O$$
$$Cr^{3+} + 3e^- \rightarrow Cr$$

Electroless plating:

The process of depositing metal from its solution over catalytically active surface area by using reducing agent without the use of electrical energy.

In electroless plating, the plating bath consists of metal ion concentration, reducing agent to reduce the metal ions into metal atom which get deposited over the surface of the article. Plating bath also consist of complexing agent, stabilizer to stabilize the bath and buffer to maintain the pH.

Electroless plating of Copper:

The plating bath solution used in electroless plating of Cu consists of

Metal ion concentration: $CuSO_4$ (12 g / L)

Reducing agent: HCHO (8 g / L)

Complexing agent: EDTA (20 g / L)

Buffer to maintain pH: Rochelle Salt (14 g/L), NaOH (15g/L)

Temperature: 25◦ C

pH: 11

Reactions:

$$\text{Cathode : } Cu^{2+} + 2e^- \rightarrow Cu$$
$$\text{Anode : } 2HCHO + 4OH^- \rightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$$
$$\text{Overallreaction: } Cu^{2+} + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2$$

Differences between electroplating and electroless plating:

Particulars	Electroplating	Electroless plating
Driving force	Direct current	Autocatalytic red-ox reaction
Reducing agent	Electrons are from DC	Electrons from reducing agent
Anode	Separate anode	Catalytic surface of substrate
Cathode	Object to be plated (Pre-treated to clean the surface)	Object to be plated (Pre-treated to make surface catalytically active)
Nature of deposit	Not satisfactory for the parts having lot of small parts	Satisfactory for all parts
Applicability	Only to conductors	Both conductors and non-conductors

Advantages of electroless plating over electroplating:

1. Semiconductors and nonconductors like plastic board can be coated.
2. Electrical power and electrical connection are not used
3. Electroless plating are pore free, harder with better resistance corrosion
4. No levellers are required for electroless plating