Application of Protective Coatings

- Protective coating provide a physical barrier between the metal and the environment.
- They not only give corrosion protection but also add to the decorative value of the article.
- Coatings are broadly divided as
  - Inorganic coatings: metallic and chemical conversion coatings.
  - Organic coatings: paints, varnishes, enamels, lacquers.
- Protective coatings are classified as:
  - Metallic coatings
  - Chemical conversion coatings
  - Organic coatings and linings
  - Ceramic protective coatings.

- The most important step before protective coatings are applied to metals is ***Surface preparation***.

Surface preparation is a process to remove rust, oxide scales, oil, grease, dust etc. If these materials are not removed, the protective coating will not be smooth, uniform, cohesive and will not adhere to the metallic surface.

Hence, mechanical and electrical methods are used to prepare the surface of the metallic article to be coated clean and free of these impurities. Mechanical cleaning, Sandblasting, Solvent cleaning, Alkali cleaning, Acid pickling & Etching are normal processes followed for surface preparation of the article to be coated.

- Mechanical cleaning:
  - Useful for removing loose scales and rust. Hammering, wire brushing, grinding, pneumatic blasting, polishing are the methods commonly used

Protective Coatings: Surface Preparation

Sandblasting:

- Fine sand or abrasive material along with air stream at a pressure of 25-100 atm is impinged on the metal surface. This will produce enough roughness for good adherence of the protective coating.
- Though the method is expensive, it is quite fast and useful

Solvent cleaning:

- Solvent cleaning is mainly used to remove oil, grease and rust from the base metal.
- Alcohols, xylene, toluene, chlorinated hydrocarbons are used.
- Hot water cleaning is followed after solvent cleaning is done.

Alkali cleaning:

- Cleaning of the metal with sodium hydroxide, trisodium phosphate, sodium silicate, soda ash etc. is carried out to remove old paint coatings soluble in alkaline medium.
- After alkali cleaning, washing is done with 1% chromic acid solution.

Acid pickling & Etching:

- Base metal is dipped inside the acid solution at higher temperature for long periods of time.
- This treatment ensures cleaning of the metal surface free from all kinds of impurities including oils, greases, rust etc.,
- H_2SO_4, HCl, HF, H_3PO_4, HNO_3 are the acids commonly used for pickling and etching.

Application of Protective Coatings: Metallic Coatings

❑ Classified into *Anodic and Cathodic coatings.*

➢ **Anodic coatings:**

→ Anodic coatings are given on cathodic metals using metals which are more anodic.

→ Zinc, Aluminium, Cadmium coatings on Iron are anodic coatings. If the coating breaks, then a galvanic couple is set up and corrosion rate gets enhanced.

→ During this process, the anodic coating gets disintegrated but it protects the cathodic base metal. Hence, the anodic metal sacrifices itself to protect the base metal.

→ This type of coating is known as *Galvanisation.*

➢ **Cathodic coatings:**

→ Cathodic coatings are given on anodic metals using metals which are more cathodic.

→ Coating of tin, chromium, nickel on iron surface are cathodic coatings. If there is a discontinuity in the coating, then galvanic couple will form with base metal as anode and the coated metal as cathode.

→ Then the process of corrosion will start by the base metal ions going into solution and the metal deteriorating.

→ To avoid this, the article is checked and re-plated periodically so that there is no discontinuity in the coating.

Metallic Coatings: Methods

I. Hot dipping
II. Electroplating
III. Electrolessplating
IV. Physical Vapor Deposition (PVD)
V. Chemical Vapor Deposition (CVD)

I. Hot dipping:

- Hot dipping process is applicable to the metals (Base metal) having higher melting point than the coating metal.
- It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.
- Exmple: Coating of Zn, Pb, Al on iron and steel surfaces
- Two types: (A) Galvanization and (B) Tinning

A. Galvanization

- Galvanization is a process in which the iron article is protected from corrosion by coating it with a thin layer of Zn. It is the anodic protection offered by the zinc.
- Uses: Galvanization is used to protect Iron from corrosion for roofing sheets, buckets, bolts, nuts, nails, pipes, wires, screws, rods etc.

B. Tinning

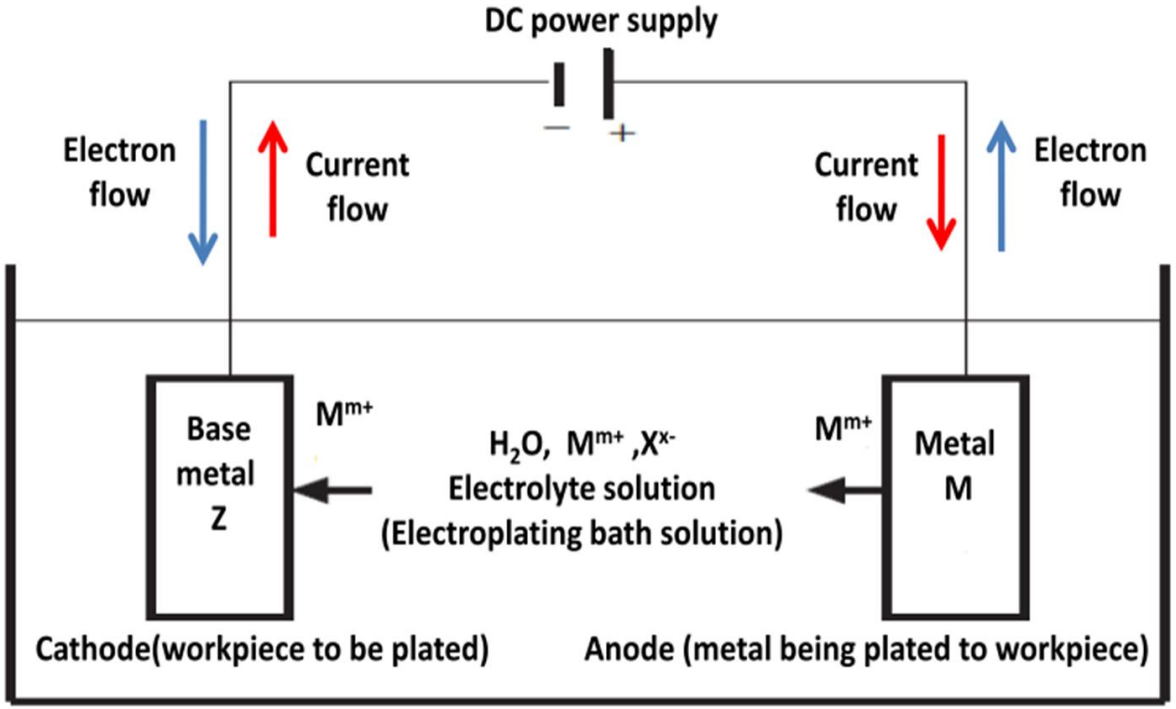
- The process of coating tin metal over the iron or steel
- Uses: Tinning is widely used for coating steel, Cu and brass sheets which are used for making containers for storing food stuff, oils, kerosene and packing of food materials. Tinned Cu sheet are used for making cooking utensils and refrigeration equipment.

I. Hot Dipping: Galvanizing vs. Tinning

Galvanizing	Tinning
A process of covering iron with a thin coat of 'Zinc' to prevent it from rusting.	A process of covering iron with a thin coat of 'tin' to prevent it from corrosion.
Zinc protects the iron sacrificially. (Zinc undergoes corrosion).	Tin protects the base metal with out undergoing any corrosion (non sacrificially)
Zinc continuously protects the base metal even if broken at some places.	A break in coating causes rapid corrosion of base metal.
Galvanized containers cannot be used for strong acidic food stuffs as Zinc becomes toxic in acidic medium.	Tin is non-toxic in nature of any medium.
Anodic protective coating	Cathodic protective coating

II. Electroplating

- It is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal
- Electroplating is done for improving corrosion resistance, wear resistance, chemical resistance, surface hardness, appearance
- Both ferrous and non-ferrous metals are plated with Ni, Cr, Cu, Zn, Pb, Al, Ag, Au, Sn etc.
- Electroplating is mainly used in automobile, aircraft, refrigerator, chemical and electrical appliances etc.



Electroplating metal M onto metal Z

- **Theory of Electroplating**

⇒ The base metal to be plated is made cathode of an electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity.

⇒ If the anode is made of coating metal itself in the electrolytic cell, during electrolysis, the concentration of electrolytic bath remains unaltered. If the anode is made of an inert material like graphite, electrolyte should be added continuously to maintain the concentration of the coating metal ions in the bath.

Important Factors of Electroplating

⇒ Cleaning of the article is essential for strong adherence of the electroplating.

➢ Scraping, grinding, sand blasting, wire brushing, solvent cleaning and acid pickling are used for surface cleaning.

➢ A well cleaned and properly pre treated surface of any material to be electroplated is necessary for obtaining the coating of long life.

⇒ Concentration of the electrolyte is another important factor.

➢ Low concentration of metal ions will give uniform coherent deposition.

➢ To maintain low conc. of metal ions, complexing agents are added to the electrolyte.

⇒ Thickness of the deposition should be optimised to get a strong & adherent deposition.

➢ For corrosion protection multiple coatings are given without any discontinuity. Thin coating is for decorative purpose.

⇒ Current density is the current per unit area of the article being plated (amps cm^{-2}). It should be maintained at optimal level to get uniform & adherent deposition.

⇒ Additives to electrolytic bath: Added in small quantities to get strong adherent deposition. Commonly used additives are gelatin, glue, glycine, boric acid etc. & brighteners for bright plating.

⇒ pH of the bath: For a good electrodeposit, the pH of the bath must be properly maintained (ranges from 4 – 8)

⇒ Method of Electroplating: Depends upon the type of metal, the size and type of article to be electro-plated. Besides, main objectives & economics are also considered.

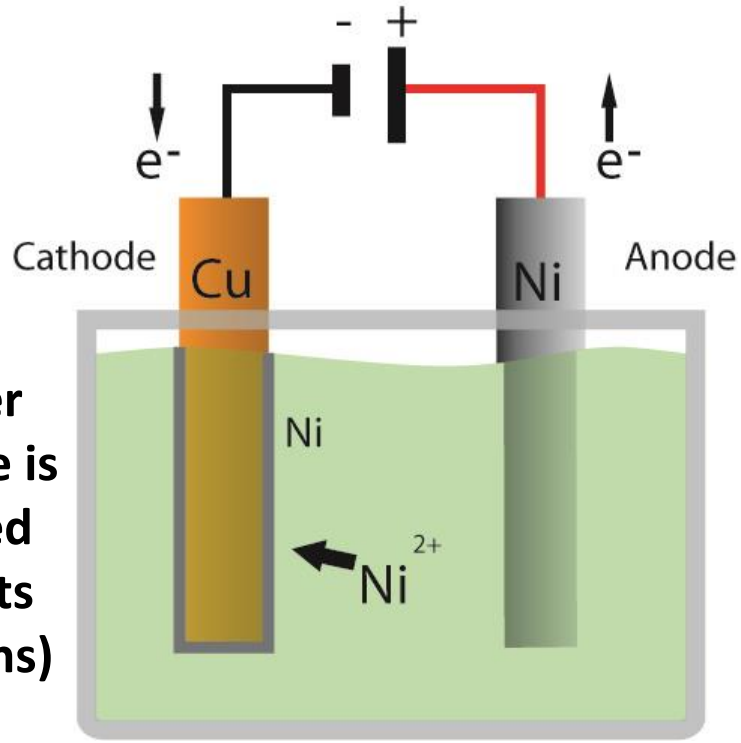
⇒ Throwing power is the ability of electrolytic cell to give a deposit of uniform thickness over the entire cathode area.

➢ Maximum throwing power can be attained when cathode has regular shape.

Electroplating: Plating Bath Solution

- It is a highly conducting salt solution of the metal which is to be plated. However, non-participating electrolytes are added to the bath solution to increase the conductivity and the throwing power.
- For sufficient throwing power, mixture of two or more electrolytes are used for electrolytic bath.
- It should be good conductor and highly soluble. It should not undergo hydrolysis, oxidation, reduction and other chemical changes.
- The level of the plating bath should cover completely the cathode and sufficient area of anode.
- Heating (if required) can be provided.
- Air sparger or nitrogen sparger is employed to introduce convection current in the plating bath solution.

Electroplating with Nickel on Copper



Copper Cathode is reduced (accepts electrons)

Nickel Anode is oxidized (gives electrons)

Ni^{2+} ions within solution become attracted to Copper cathode

III. Electrolessplating

- Electrolessplating is the controlled autocatalytic deposition of a metal on a substrate (conductor/Nonconductor) from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy. This process is also called autocatalytic plating, since it takes place on catalytic surface.
- The metallic ions (M^+) are reduced to the metal with the help of reducing agents (R^-). When the metal (M) is formed, it gets plated over a catalytic surface.

$$M^+ + R^- \rightarrow M + R$$

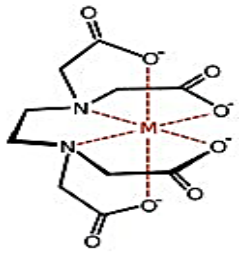
- Typically, sodium hypophosphite is used as a reducing agent. Also, formaldehyde, hydrazine, borohydride, amine boranes, and their derivatives could be utilized

Copper electrolessplating

Two subreactions (reduction and oxidation):

- $(CuEDTA)^{2-} + 2\ e^- \rightarrow Cu + EDTA^{4-}$ $\quad E^o = -0.216$ V
- $2\ HCHO + 4\ OH^- \rightarrow H_2 + 2\ HCOO^- + 2\ H_2O + 2\ e^-$ $\quad E^o = -1.14$ V

Formaldehyde



Overall reaction:

$$(CuEDTA)^{2-} + 2\ HCHO + 4\ OH^- \rightarrow Cu + H_2 + 2\ \underset{\text{Formate}}{HCOO^-} + 2\ H_2O$$

$E^o = E^o(\text{reduction}) - E^o(\text{oxidation}) =$

$-0.216\ V - -1.14\ V = 0.924\ V$

$\rightarrow \Delta G^0 = -zFE^0 < 0$

→ the process is spontaneous and the solution metastable

→ homogeneous precipitation is kinetically inhibited

→ the heterogeneous deposition reaction is catalyzed

The electrolessplating involving a nickel sulfate bath

$$NiSO_4 + NaH_2PO_2 + H_2O \xrightarrow[\text{catalyst}]{\text{heat}}$$

$$Ni\ Plating + NaHPO_3 + H_2SO_4$$

III. Electrolessplating

- **Advantages of electrolessplating:**
  - Electrical energy is not required.
  - Even intricate parts (of irregular shapes) can be plated uniformly.
  - There is flexibility in plating volume and thickness. The process can plate recesses and blind holes with stable thickness.
  - Chemical replenishment can be monitored automatically.
  - Plating on articles made of insulators (like plastics) and semiconductors can easily be carried out.
  - It is a pore free coatings with very high hardness, corrosion resistance and wear resistance values.

- **Differences**

	Electroplating	Electrolessplating
Driving force	Electric current	Autocatalytic reduction reaction
Electrodes	Separate anode and cathode	Catalytically active surface
Applicability	Deposition can't be made on non-conductors such as plastics, ceramics etc.	Deposition can be made on non-conductors such as plastics, ceramics etc.
Throwing power	Low	High
Nature of deposit	Pure metal	Metal contaminated with reducing agents and oxidizing agents
Additives	Levelers are added.	Levelers are not required.