MODULE : 2

CORROSION & METAL FINISHING

The word Corrosion is derived from Latin word CORRODERE, is defined as “the destruction or deterioration and consequent loss of metals or alloys through chemical or electrochemical attack by the surrounding environment”. i.e., Transformation of pure metal into undesired metallic compounds.

\[\text{Metal} \rightarrow \text{Metal ore}\]

The primary factors that initiate corrosion on metals are atmospheric air, water and conducting surface of the metal.

e.g., i) Rusting of iron (formation of hydrated ferric oxide \((\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O})\), a reddish brown scales), ii) Green scales on copper vessels [It is due to the formation of basic cupric carbonates \((\text{CuCO}_3 + \text{Cu} (\text{OH})_2)\)]

Corrosion of metal occurs either by direct chemical attacks or by electrochemical attack on the metal by the corrosive environment.

- If the corrosion takes place due to direct chemical attack (in the absence of moisture) only in presence of atmospheric gases such as \(\text{O}_2\), \(\text{N}_2\), \(\text{H}_2\text{S}\), \(\text{SO}_2\) is known as **dry corrosion**.
- If the corrosion of metal takes place due to electrochemical attack in presence of moisture or a conducting medium such corrosion is known as **wet corrosion or electrochemical corrosion**.

**Electrochemical theory of corrosion:**

- Most of the corrosion takes place on the basis of electrochemical reactions on the surface of metal. Electrochemical theory of corrosion can be explained by taking iron as an example.

According to electrochemical theory corrosion of metal takes place due to the formation of anodic and cathodic regions on the same metal surface or when the two metals are in contact with each other in a corrosive medium.

- At anodic region, oxidation takes place so that metal is converted into metal ions with the liberation of electrons.

\[
\begin{align*}
\text{M} & \rightarrow \text{M}^{n+} + n\text{e}^- \\
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}
\end{align*}
\]

Cathodic reactions:

a) Liberation of Hydrogen

(i) If the medium is acidic and in the absence of \(\text{O}_2\)

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2
\]
(ii) If the medium is neutral or alkaline in the absence of \( O_2 \).

\[
2H_2O + 4e^- \rightarrow 2OH^- + H_2
\]

b) Absorption of oxygen

(i) If the medium is acidic and in the presence of \( O \).

\[
4H^+ + O_2 + 4e^- \rightarrow 2H_2O
\]

(ii) If the medium is neutral or alkaline and in the presence of \( O_2 \).

\[
2H_2O + O_2 + 4e^- \rightarrow 4OH^-
\]

The metal ions (Fe\(^{2+}\)) liberated at anode and some anions (OH\(^-\)) formed at cathode diffuse towards each other through the conducting medium and form a corrosion product (hydrated ferric oxide) or rust.

\[
2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2
\]

\[
2Fe(OH)_2 + O_2 + (n-2)H_2O \rightarrow Fe_2O_{3n}H_2O \text{ (Oxide rust)}
\]

**Factors affecting rate of corrosion:**

Several factors which affect the rate of the corrosion are divided into two main factors

1. Primary Factors (factors related to the metal)

**Primary factors:**

1. **Nature of the metal (Electrode Potential):** The tendency of the metal to undergo corrosion is mainly dependent on the nature of the metal. In general, the metal with lower electrode potential is more reactive and more susceptible for corrosion, and metal with high electrode potential is less reactive and less susceptible for corrosion. 

   E.g., metals like K, Na, Mg, Zn etc have low electrode potential and undergo corrosion very easily, whereas noble metals like Ag, Au, Pt have higher electrode potential, their corrosion rate are negligible. 

   When two metals are in contact, it is the difference in their potential that decides the rate of corrosion. Larger the difference in potential larger will the rate of corrosion.

2. **Surface state of the metal (or) Nature of the corrosion product:** The corrosion product is usually the oxide of the metal; the nature of the product determines the rate of further corrosion process.
If corrosion product is highly insoluble, stable, stoichiometric, non-porous with low ionic and electricity conductivity, the formed layer prevents further corrosion by acting as protective barrier.

Ex: Corrosion product of Al, Cr, Ti etc.,

If corrosion product is soluble, unstable, non-stoichiometric and has appreciable conductivity, the formed layer cannot prevent further corrosion.

Ex: Corrosion product of Fe, Zn, Mg etc.

3. **Anodic and Cathodic area (area effect) or relative size of anode and cathode:**

- Rate of corrosion depends upon how fast the electrons are consumed at cathode.
- If the anode area is small and cathode area is large, the rate of corrosion increases. Because at anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed.
- This process makes the anodic reaction to takes place at its maximum rate thus increasing the corrosion rate.
- For example, a broken coating of tin on the iron surface enhances corrosion rate of iron. Tin is cathodic to iron and the small exposed part of iron acts as anodic region and remaining large tin coated surface acts as cathodic region.

4. **Polarization of electrodes:**

Polarization is defined as the deviation of the potential of an electrode from the open circuit potential due to irreversible reactions around the electrode. Polarization causes the potential of the cathode to become more anodic and that of anode to become more cathodic. Therefore, the potential difference between the electrodes decreases steadily and the amount of current in the closed circuit decreases thereby lowers the rate of corrosion.

The corresponding value of the current at this state is corrosion current.

\[ I_{\text{corr}} = i_a - i_c \]

Where, \( i_a \) is anodic current density

\( i_c \) is the cathodic current density.

NOTE: Greater the extent of polarization of either anode or cathode or both, smaller is the corrosion current and hence lower is the rate of corrosion.

There are three types of polarization.

a) If the anode alone undergoes polarization the rate of corrosion is said to be control by anodic polarization where the corrosion current is largely determined by the potential at the anode.
b) If the cathode alone undergoes polarization, the rate of corrosion is said to be controlled by cathodic polarization where the corrosion current is largely determined by the potential at the cathode.

c) If both the electrodes undergo polarization, it is under mixed control polarization.

**SECONDARY FACTORS** (Factors related to environment):
1. **pH of the medium:** Usually higher acidic nature (low pH) higher is the rate of corrosion.
At lower pH, severe corrosion occurs in the absence of air due to the continuous evolution of $\text{H}_2$ at cathode. However metals like Al, Zn etc undergo fast corrosion in highly alkaline medium.

2. **Temperature**: On increasing the temperature rate of corrosion process also gets increases because Conductance of the aqueous medium increases hence rate of diffusion also increases.

3. **Humidity**: Most of the metals corrode faster in a humid atmosphere than in dry air. There is a particular value of humidity called ‘Critical Humidity’. It is the relative humidity above which corrosion rate steeply increases.
   - Humidity helps in the formation of electrochemical cell on the surface and dissolution of gases like $\text{O}_2$, $\text{CO}_2$, $\text{SO}_2$ etc

4. **Presence of impurities**: The presence of certain impurities in the atmosphere enhances the rate of corrosion. For example when $\text{SO}_2$ is present as impurity in the atmosphere; it combines with moisture or rain water forming sulfuric acid.

5. **Electrical conductivity of the corrosive medium**: As the conductivity of corrosion medium increases, the corrosion rate also increases. Higher the conductivity of the medium, faster the ions migrate between the anodic and cathodic regions of the corrosion cell.

**GALVANIC SERIES**: Standard electrode potential ($E^0$) values cannot be used satisfactorily to corrosion tendency when alloys and passive metals are under consideration.

In electrochemical series metals are arranged in an increasing order of their electrode potential values ($E^0$). A metal placed higher in the series is more anodic and corrode faster than the one below it in the series.

Galvanic Series: Magnesium
   - Alluminium
   - Zinc
   - Iron
   - Nickel
   - Tin
   - Copper
   - Stainless Steel
   - Silver
   - Gold
But for engineering applications many alloys are used under various environments. Corrosion behavior of such alloys cannot be predicted by electrochemical series. To overcome this limitation galvanic series was introduced.

Corrosion characteristics of metal and alloys can be studied using galvanic series.
Greater the difference in their position in the galvanic series faster will be the rate of corrosion.

**Types of Wet Corrosion:**
1. Differential metal corrosion (Galvanic corrosion)
2. Differential aeration corrosion
3. Stress corrosion

1. **Differential Metal Corrosion**:
   This occurs when two dissimilar metals are in contact with each other in a corrosive conductive medium. The two metals differ in their tendencies to undergo corrosion. A potential difference is set up resulting in a galvanic current.

   The metal with lower electrode potential (more active metal) acts as anode and the metal with higher electrode potential acts as cathode. The potential difference between the two metals is the driving force for corrosion. Higher the difference higher is the rate of corrosion. The anodic metal undergoes corrosion whereas cathodic metal remains unaffected.

   e.g., when iron is in contact with copper, iron has lower electrode potential acts as anode and undergoes oxidation as,
   \[
   Fe \rightarrow Fe^{2+} + 2e^{-} \\
   2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2
   \]

   In an oxidizing environment, the insoluble Fe(OH)₂ oxidized to ferric oxide as following reaction
   \[
   4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 2(Fe_2O_3 - 3H_2O)
   \]

   yellow rust

   Whereas copper which is having higher electrode potential acts as cathode remain unaffected. The rate of galvanic corrosion depends upon potential difference between anodic and cathodic metals, ratio of anodic and cathodic area and environmental factors and tendency of the metal to undergo passivity etc.
2. DIFFERENTIAL AERATION CORROSION:

Different types of aeration corrosion occur when metal surface is exposed to the differential air or oxygen concentration, which develops galvanic cell and initiates corrosion.

- The part of the metal exposed to lower oxygen concentration acts as anode and the part of the metal exposed to higher concentration acts as cathode, so that poorly oxygenated region undergoes corrosion.
- At anode (less oxygen concentration) oxidation of metal takes place:

\[
M \rightarrow M^{n+} + ne^{-}
\]

At cathode (more oxygen concentration) reduction of metal takes place:

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^{-}
\]

Some common examples for aeration corrosion as follows:
1. Part of nail inside the wall, being exposed to lower concentration than the exposed part, undergoes corrosion.
2. Window rods inside the frame suffer corrosion but not the exposed region.
3. Paper pins inside the paper gets corrode and the exposed part is free from corrosion.
4. Metals under extraneous matter i.e., dirt, dust, sand or any other impurities undergo corrosion.

Types of differential aeration corrosion:

a). Water line corrosion:

This is a case of differential aeration corrosion commonly observed in steel water tanks, ocean going ships etc. in which portion of the metal is always under water

- The part of the metal below the water line is exposed to only to dissolved oxygen while the part above the water is exposed to higher concentration of oxygen.
- Thus the metal part below the water line acts as anode where as above the waterline acts as cathode and process of corrosion starts.

The metal just below the water line is more anodic and the one which is more oxygenated acts as cathode and unaffected.
Ex: Consider a piece of Zn metal is partially immersed in a dilute solution of NaCl and the solution is not agitated properly. The part of metal above and closely adjacent to the waterline are more oxygenated because of easy access of air and hence become cathodic. The part of Zn metal immersed to the greater depth which have less access of air become anode. Hence a difference in potential between the electrode is created which causes a flow of current between the two differentially aerated areas of the same metal and causes corrosion at anode.

b) **Pitting Corroison**:

Pitting corrosion is a highly localized and accelerated corrosion. Pitting corrosion is generally initiated by the deposition of extraneous matter such as sand, water droplets, dirt, dust etc., on a metal surface due to the breakdown of the protective film on the surface of a metal.

The portion covered by the dust will not be well-aerated area compared to the exposed surface hence the covered surface becomes anodic with respect to the surface exposed. In presence of conducting medium (moisture) corrosion starts below the dust part and forming a pit.

- Once pit is formed the ratio of corrosion increases, because of the formation of smaller anodic and larger cathodic area intense corrosion takes place.
Pitting corrosion is one of the most destructive form of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. Because of the small sizes of the pits it is highly difficult to identify the pitting corrosion.

**STRESS CORROSION:**

Stress corrosion of the metal formed by the combined effect of a tensile stress and a specific corrosive environment. During stress corrosion, the metal or alloy is virtually unaffected over most of its surface, while fine cracks progress through it normal to the direction of tensile stress.

The stress on the metal may be internal or external and stress is due to some mechanical or service conditions. When a metal is subjected to the mechanical process such as pressing, hammering, bending, welding etc causes stress. Stress produces strains resulting in localized zones of increased energy. These zones are very active and are attacked even by mild corrosive agents.

The metal atoms under stress are always at higher energy level so acts as anode and stress free parts of metal acts as cathode. As a result of this corrosion cell is formed with the stressed part acting as anode and the stress free part acting as cathode. But best example for stress corrosion is caustic embrittlement and season cracking.

**Caustic embrittlement:** It is a form of stress corrosion takes place in boilers operating at high temperature and pressure. Caustic embrittlement focus at stressed part of boilers such as cracks, rivets, bents, joints etc.
Water used in boilers generally contain Na₂CO₃ (used for softening of hard water) which is hydrolysed at high temperature at NaOH.

\[
\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2
\]

The NaOH produced gets accumulated in stressed regions of boiler. When the concentration of NaOH reaches sufficient level (> 10%) it attacks iron, leading to corrosion and boiler failure.

\[
2\text{NaOH} + \text{Fe} \rightarrow \text{Na}_2\text{FeO}_2 + \text{H}_2
\]

\[
3\text{Na}_2\text{FeO}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 6\text{NaOH}
\]

- Once NaOH is regenerated in the process and its concentration is kept on increasing maintaining a required environment. Thus corrosion process develops cracks and makes the metal brittle by the deposition of the product.
- The continuation of caustic embrittlement of boiler often results in boiler explosion.

**CORROSION CONTROL:**

Corrosion of a metal is a natural spontaneous process, by which metal is converted into a more stable compound so that corrosion control is more realistic than corrosion prevention. In general preventing the formation of galvanic cells can control corrosion.

The methods used to control corrosion are as follows:

Corrosion of metal can be controlled by preventing the formation of anodic areas in metals. The more common used are given below:

1. **Inorganic coating**
   - i) Anodizing
   - ii) Phosphating

2. **Metal coating**
   - i) Anodic Metal Coating (Galavising)
   - ii) Cathodic Metal Coating (Tinning)

3. **Cathodic Protection**
   - i) Sacrificial Anode Method.
   - ii) Impressed current method.

**INORGANIC COATINGS (surface conversion coating) or chemical conversion coating:**

- Here a surface layer of the metal is converted into a stable compound by chemical or electrochemical reactions, which forms a barrier between the base metal and corrosion environment.
These types of coating are different compared to that of metal coating because they are integral part of the metal itself.

And in addition to corrosion resistance they also provide increased electrical insulation and physical appearance of the metal.

In surface conversion coating two important types are

1. **ANODIZING**:
   Anodizing is the process of formation of thin and compact layer of metal oxide over base metal through electrolysis.
   Anodizing usually carried out on non-ferrous metals like Al, Cr, Ni, etc or their alloys by anodic oxidation process in which base metal is made as anode, in an electrolytic bath of suitable composition and by passing direct current.

   For example: Anodizing of aluminum: When an aluminum is undergoing chemical or electrochemical reaction, alumina (Al₂O₃) is formed on the surface of aluminum by using oxidizing electrolyte like H₂SO₄, Chromic acid, Oxalic acid etc., about 35°C under moderate current density.
   Electrolytic bath contains the following chemicals:

   Over all reaction:
   
   Anode reaction : \(2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\)
   
   Cathode reaction : \(6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\)

   Al₂O₃ formed will be porous in nature, the pores are sealed by dipping in hot water. During the sealing processes Al₂O₃ absorbs moisture to form Al₂O₃·H₂O. These oxide films are protective, corrosion resistant and electrically insulating in nature.

   **Advantages:**
   Anodized coatings are somewhat thicker than the natural oxide films, so they possess improved resistance to corrosion as well as mechanical injury.
   
   1. They are used for decorative purpose (as coloring agents)
   2. It is also used in satellite applications for their protection in space environment.

2. **PHOSPHATING**: It is process in which phosphate coatings are generally obtained on steel surface by converting surface metal atoms into their phosphates by chemical or electrochemical reaction. The phosphating bath containing three essential components
   
   1. Phosphoric acid
   2. Primary phosphate like Fe, Mn, or Mg phosphate.
   3. Accelerator such as nitrates, nitrites hydrogen peroxide (oxidizing reagent)
The mechanism of phosphating involves following steps.
1) First dissolution of the metal as metal ions.
2) Metal ions reacting with phosphate ions to form a metal phosphate.
3) Deposition of the metal phosphate on the surface of the metal.

\[ 3\text{Fe} + 2\text{H}_3\text{PO}_4 \rightarrow \text{Fe}_3(\text{PO}_4)_2 + 2\text{H}_2 \]

**Zinc phosphating process:**
Iron metal is immersed into a phosphating solution containing Zn\(^+\) ions and the following chemical reaction takes place,
Iron metal dissolves in the phosphoric acid solution:

\[ 3\text{Fe} + 6\text{H}^+ \rightarrow 3\text{Fe}^{2+} + 3\text{H}_2 \]
Consumption of \(\text{H}^+\) for the reaction raises \(p^\text{H}\) of the solution in the layer adjacent to the metal surface. Solubility of zinc phosphate decreases at higher \(p^\text{H}\), resulting in the precipitation of the salt (ZnPo\(_4\)) on the metal surface which prevent corrosion.

\[ 3\text{Zn}^{2+} + 2\text{Po}^{3+} \rightarrow \text{Zn}_3(\text{Po}_4)_2 \]

**Application:** As undercoating before painting of automotive bodies, refrigerators, washing machines etc.

**Metal coating:**
Deposition of a protective metal over the surface of the base metal is called metallic coating. The method can be applied by electrodeposition, flame spraying, cladding, hot dipping etc.
On the basis of coating there are two classes:
1. **Anodic coating (Galvanizing):** It is produced by coating a base metal with more active metal which is more anodic with respect to the base metal for eg: Iron is coated with Zn, Mg, Al etc.,
   - Galvanisation is one of the best example for anodic coating.
2. **Galvanisation:** It is a process of coating a base metal (iron) with zinc (Zn) metal. This process usually carried out by hot dipping method.
**Process:** First the base metal surface is washed properly with organic solvents to remove organic matter (like oil, grease etc) on the surface.

2. Afterwards it is washed with dil. H₂SO₄ to remove inorganic matter (like rust).
3. Finally the base metal is well washed with water and air-dried.
4. The base metal then dipped in a bath of molten zinc maintained at 425-430°C and covered with a flux of NH₄Cl to prevent the oxidation of molten zinc.
5. Then excess zinc on the surface is removed by passing through a pair of hot rollers so that a proper thin coating is obtained.

**Application:** Galvanized articles are mainly used in roofing sheets, fencing wire, buckets, bolts nuts, pipes and tubes etc. but galvanized articles are not used for preparing and storing food stuffs. Since zinc dissolves in dil. Acids and become toxic.

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**ORGANIC COATING:**

Coating of inert organic materials like paints, varnishes and lacquers on metallic surface to protect the metal. The organic coating serves as a barrier between the metal surface and corrosive environment.

The requirements of a good organic coatings are as below

i) The organic coating should adhere tenaciously to the metal surface and should improve its physical appearance.

ii) The film formed should be uniform, continuous and act as a barrier to air and water.

iii) It should be chemically inert.

iv) Should have reasonably long life.
v) Should be easily available with low cost and properly applicable.

**CATHODIC PROTECTION:**
It is a method of protecting the metal or alloy from corrosion and no part of it is allowed to act as anode. Or it is a technique of offering protection to a specimen against corrosion by providing electrons from an external source.

There are two methods for providing electrons for cathodic reactions there are

1. **Sacrificial anode method:**
2. **Impressed current (voltage) method**

1. **Sacrificial anode method:**
The method involves the use of more active metals as sacrificial anode in contact with specimen (like iron, copper or brass).
The active metals like Zn, Mg, Al, and their alloy acts as an auxiliary anode and undergoes preferential corrosion protecting the metal structure. Here the anode metals are sacrificed to protect the metal, the method is known as sacrificial anode method.

   This form of CP is not practical for large scale installation where long-term corrosion protection is required. Exhausted anodes are replaced by new ones as and when required.

   For example: Mg or Zn block connected to a buried oil tank and Mg bars are connected to ocean going ships.

   ![Diagram of cathodic protection](image)

   **Applications:**
   1. Sacrificial anode methods are simple with low installation cost.
   2. Sacrificial anode method does not require power supply but involves recurring expenditure of replacement of consumed anodes.
Impressed current cathodic protection (ICCP)
The principle of impressed current cathodic protection is in connecting an external anode to the material to be protected from corrosion and passing of an external (impressed) electrical DC current.

- The structure to be protected should be made cathode and connected to negative terminal of a D.C source and an auxiliary metal or graphite is connected to the positive terminal of the battery which acts as anode.

These impressed current anodes are also known as dimensionally stable anode or insoluble anodes, (platinised Ti Or Pb, Graphite rods are used) they are resin bounded or back fill (carefully insulated to prevent current leakage, which improves electric contact between anode and environment).

- The main structure being cathode does not undergo corrosion, and anode being inert remains unaffected.

Applications: CP systems are most commonly used to protect steel pipelines and storage tanks, steel pier piles, oil pipe lines. CP has been proven an effective method for reducing corrosion and preventing stress corrosion cracking in large metal structures.

This method is simple, can protect large metal area with low maintenance cost but expensive, because it needs high current and it is difficult to maintain to uniform current over the entire metal surface.
UNIT 2 : METAL FINISHING

INTRODUCTION:
The term metal finishing involves many processes carried out to modify the surface properties of a metal by depositing a layer of another metal or a polymer. No single metal or alloy can have all ideal properties like corrosion resistance, wear resistance, mechanical, electrical and thermal properties. Therefore metal finishing is one of the methods employed to improve the properties.

Metal Finishing is a process of deposition of a layer of one metal on the surface of substrate metal.

Important electrochemical metal finishing techniques are: Electroplating and Electroless plating process.

TECHNOLOGICAL IMPORTANCE :
Technological importance of metal finishing is in imparting certain additional properties to the materials.
1) To offer corrosion resistance.
   To provide decorative appearance.
2) To impart wear (appearance, decorative, protection) resistance.
3) To provide electrical and thermal conducting surface.
4) To impart thermal resistance.
5) To offer the surface thermal and optical reflectivity.
6) To enhance chemical resistance.
7) To improve mechanical strength (hardness).
8) Manufacturing electrical and electronic components like printed circuit boards, capacitors etc..

PRINCIPLES GOVERNING THE PROCESS OF METAL FINISHING:
The three important factors that govern the process of electroplating and electrolysis are:
Polarization, decomposition potential and over potential.
1) POLARIZATION:
Definition: “It is a process where there is a variation of electrode potential due to slow supply of metal ions from bulk of the solution to the vicinity of the electrode”
It is classified as follows:

1. **Variation of concentration polarization**
   During electrolysis, metal ions in the vicinity of cathode get reduced. If metal ions are not supplied sufficiently, the concentration of metal ions at cathode decreases, this leads to decrease in electrode potential as evident from Nernst Equation.
   \[ E = E^0 + \frac{2.303RT}{nF} \log M^{n+} \]
   Concentration polarization is generally overcome by stirring the electrolyte.
   Polarization depends on several factors:
   1) Size, shape and composition of electrode.
   2) Electrolyte concentration and its conductivity.
   3) Temperature.
   4) Products formed at electrodes.
   5) Rate of stirring of electrolyte.

2. **Activation Polarization**:
   The deposition of metal on cathode involve several steps and if any one of the steps involved is slow, it will result in polarization. Activation polarization can be overcome by applying excess voltage or Overvoltage.

2) **DECOMPOSITION POTENTIAL (E_D)**:
   **Definition**: “The minimum external voltage that must be applied in order bring about continuous electrolysis of an electrolyte”
   Determination: In the electrolysis of water, at low voltage no reaction occurs and there is slight increase in current on increasing voltage. On increase the voltage above 1.68V, there is an abrupt increase in the current and sudden evolution of H\(_2\) at cathode and O\(_2\) at anode takes place.
   The reaction product H\(_2\) and O\(_2\) set in galvanic cell leading to a back emf, E_{back} which opposes applied voltage.
   \[ E_{back} = E_{cathode} - E_{anode} = 1.23V \]
   Decomposition Potential( E_D ) , for electrolysis splitting of water is calculated using equation,
   \[ E_D = E_{back} + \eta \]
   \[ E_D = 1.23V + 0.45V = 1.68V \]
   The applied minimum voltage 1.63V is the decomposition voltage for the electrolysis of water.
3) OVER POTENTIAL (VOLTAGE):  
• In general, for continuous electrolysis to take place, the applied voltage should be equal to or slightly more than the decomposition potential. In few cases even when voltage decomposition potential is reached, electrolysis will not occur and sometimes the applied voltage has to exceed the theoretical voltage by 1V for continuous electrolysis. This is known as over potential or over voltage.

   Over voltage = Experimental voltage – Theoretical voltage  
   = 1.63V – 1.23V  
   = 0.45V

   Overvoltage for electrolytic splitting of water is formed.

• DEFINITION: “The excess voltage that has to be applied above the theoretical decomposition potential for continuous electrolysis.”

   Over potential for a given electrolyte depends on:
   1) Nature of electrodes.
   2) Nature of substance deposited.
   3) Current density
   4) Temperature
   5) Rate of stirring of electrolyte

   The hydrogen over voltage is the over voltage required for the liberation of hydrogen at cathode during electrolysis. This is important in electroplating process.

ELECTROPLATING:

“Electroplating is the deposition of a metal, over the surface of another metal or alloy or any conductor by the process of electrolysis.”

In this process a metal is deposited on another metal or alloy by passing a direct current through an electrolyte solution containing metal ions to be deposited.

THEORY OF ELECTROPLATING:

The article to be plated is made as cathode (substrate) and the metal to be plated on cathode is made as anode. Electroplating is carried out in an electrolytic cell. It consists of two electrodes the metal to be coated is taken as cathode and connected to negative terminal of a DC power source. Anode is connected to positive terminal of the power source the electrodes are dipped in an ionic solution of the metal to be plated on applying direct, cations move towards cathode and get reduced to metal atoms and deposited over cathode.

   Cathode reaction $M^{n+} + ne^- \rightarrow M$
A ions move towards anode and get oxidized at the anode surface if the anode is inert. If the anode is dissolvable, the electrode itself gets oxidized.

Anode reaction $M \rightarrow M^{n+} + ne^-$

Hence, plating is a redox reaction, where oxidation occurs at anode and reduction at cathode.

Commonly used coating metals are Zn, Cu, Cr, Ni, Ag, Pt, Au etc...

FACTORS INFLUENCING THE NATURE OF ELECTRO DEPOSIT:
The nature of electro deposit is affected by several factors, the important among them are:

1) CURRENT DENSITY:
   It is defined as the current per unit area of electrode surface. It is expressed in mill amperes per square centimeter ($mA/cm^2$) or amperes per square meter ($A/m^2$).
   - At low current density, surface diffusion is fast as compared to the electron transfer, hence metal is deposited slowly and takes long time for deposition.
   - At high current density (when current density is increased), surface diffusion may not reach most favourable portions. As mass transport of ions from bulk of the solution predominates, it results in a rough, powdery, loose deposit. This also causes hydrogen evolution on the surface of cathode, this results in dispersed powders containing oxides and hydroxides of the metal, hence a spongy and burnt deposit is formed.
   - Hence for a particular deposition optimum current density is determined and used to get a good deposit.

2) $P_{H}$ OF ELECTROLYTIC BATH:
   - At low $P_{H}$ values, evolution of hydrogen gas occurs on the cathode, which results in burnt deposit.
   - At higher $P_{H}$ values, the electrode surface gets coated with insoluble hydroxides.
   - Therefore $P_{H}$ range of 4 to 8 is used i.e., slightly acidic or slightly basic (alkaline). The $P_{H}$ is maintained by using a suitable buffer. eg: Borate buffer is used in Ni plating and citrate buffer in gold plating.

3) THROWING POWER OF PLATING BATH:
   “The ability of a plating bath to give a uniform and even deposit on the entire surface of object is measured by its throwing power”

   This is particularly important in objects of complex shapes. eg: plating in holes and breakings (bends) takes place less uniformly than on even surfaces.
Throwing power is said to be good if the distribution of deposit is uniform, irrespective of the shape of object. The throwing power of a plating bath is determined using **Haring-Blum cell**.

- Haring-Blum cell consists of plating bath solution and anode at the center cell.
- Two cathodes are placed at distances $d_1$ and $d_2$ from anode ($d_1 > d_2$) as shown in figure.
- The surfaces of two cathodes away from anode are insulated (deposition occurs only on the surface of cathodes which is towards anode).
- Electroplating process is carried out and the weights $W_1$ and $W_2$ of metal deposited on cathodes are noted.
- Then throwing power can be calculated by using the equation:

$$\% \text{ of throwing power} = 100 \left( \frac{x - y}{x + y - 2} \right)$$

- When the amount deposited is same ($W_1 = W_2$), irrespective of the placement of electrodes, throwing power is 100% and is considered to be very good.

**4) TEMPERATURE:**
- At **high** temperature, the rate of evolution of hydrogen gas at cathode **increases**, this results in **spongy and loose deposit**, also sometimes causes the decomposition of organic additives.
- At **low** temperature, electroplating results a **powdery deposit**.

Hence **moderate temperature is preferred**, at this temperature the surface diffusion is more than hydrogen evolution. Hence plating of metals is generally carried out between 35$^\circ$C and 60$^\circ$C.

**5) CONCENTRATION OF METAL ION AND ELECTROLYTES:**
- The metal ion concentration is **normally kept low** (1-3 mol dm$^3$) because firm and adherent deposits can be obtained.
- If the metal ion concentration is **high**, mass transfer of ions occurs from bulk electrolytic solution to the electrode surface, this results in **powdery deposit**.
- Electrolytes are added in **high concentration**, to **increase the conductivity of plating bath**. These electrolytes do not participate in the electrode reactions but increase the conductivity and control the change in $P^H$. 
6) CONCENTRATION OF METAL SALT: 
The metal salt concentration is kept high, because a high current density can be employed at high metal content in the solution. In such type of bath the limiting current density is raised; the bad effects of high current density are thus shifted to higher values of current density.

ADDITIVES (ORGANIC ADDITIVES): These are the substances added to bath to improve the nature of deposit i.e., to modify the structure, morphology and properties of electro deposit. This include:

1) Complexing Agents: These are added to maintain low metal ion concentration. The metal ion is converted into a complex ion by the addition of suitable complexing agent to get more adherent deposit. Complex ions are used,
1) To maintain low metal ion concentration in solution (plating bath).
2) To improve throwing power of plating bath.
3) It helps to carry out plating at lower potential.
4) To prevent the chemical reaction between cathode metal and plating ions.

2) Brighteners: These are the chemical substances that are added to plating bath to get bright and lustrous (glowing) deposit. For a deposit to be bright, the light falling on the surface should be reflected. This happens when the grain size (single particle size) is lower than the wavelength of incident light. Brighteners are added to produce microscopically fine deposits. Their concentration must be maintained at an optimum range. Commonly used brighteners are: molecules containing C≡N, N=C=S, C=O groups (eg: thiourea and coumarin).

3) Wetting Agents: During electroplating hydrogen is evolved at the cathode. Wetting agents are added to release the gas bubbles from the surface. They also improve the levelling and uniformity of the deposit. In the absence of wetting agents the gas bubbles may get entrapped within the plated metal and try to escape after plating, this may cause the breakage in deposit.
   Eg: sodium lauryl sulfate.

4) Levellers: Plating takes place rapidly on certain regions such as on dislocations where the diffusion of ions is faster resulting in a deposit of uneven thickness. Levellers help to produce a uniform deposit on the surface by getting adsorbed at regions where rapid deposition occurs. Thus the adsorbed additives reduce the rate of electron transfer at such places. Many brighteners acts as levellers.
   Eg: Sodium allyl sulphonate is used as leveler for Ni deposition.
5) Structure modifiers: They are also called as stress relievers. They alter the structure of electrodeposit and modifies the properties of electrodeposit. Electrodeposits are associated with internal stress (due to lattice misfit), if this stress level is too high, it may lead to cracking of deposit. Eg: Saccharin is added as stress reliever.

**PLATING PROCESS:**
The plating process is carried out by pretreating the object followed by electrolysis.

**PRETREATMENT (SURFACE PREPARATION):**
It is necessary to clean surface of metal electroplating in order to get a good deposit. The impurities found on the surface may be grease, oxide film, oil, dust etc…

Various methods are available to clean the surface of metal:
1) **Solvent cleaning:** Organic solvents (like CCl₄, toluene, trichloro ethylene, etc) are used to remove impurities like oil, grease, etc from the surface of metal. The process involved is: solvent is vapourized by heating process, these vapours are then made to condense on the metal surface to be cleaned. The condensed liquid dissolves and washes away the impurities present.
2) **Acid cleaning**(pickling): It is used to remove oxides. After the removal of organic impurities, the substrate is immersed in dilute HCl or H₂SO₄, this removes oxides.
3) **Alkali cleaning:** This method is employed to remove old paint from the metal surface using alkali solutions (i.e., solution of NaOH, sodium silicate, sodium carbonate etc..) Alkali reacts with oil, grease and removes it. Combination of alkali with a chelating agent such as EDTA, sodium citrate, etc.. this cleans the metal surface.

**ELECTROPLATING OF CHROMIUM:**
Before electroplating process the surface on which deposition is carried out is to be pretreated, i.e., substrate is subjected to solvent cleaning to remove organic impurities (oil, grease, etc..). Then followed by acid cleaning, to remove the inorganic impurities (oxide films) present on the surface.

**In electroplating of chromium two types of chromium are employed:**
**decorative and hard chromium.**
Hard Cr plating involves deposition of a thick coating of Cr directly over the substrate (thickness→2.5 to 300 m).
Plating bath contains chromic acid, during electroplating of Cr, Cr(VI) is reduced to Cr(III) in presence of $\text{SO}_4^{2-}$ catalyst (furnished by $\text{H}_2\text{SO}_4$)

<table>
<thead>
<tr>
<th>Cr plating</th>
<th>Decorative Cr</th>
<th>Hard Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Bath composition</td>
<td>100:1 chromic acid and $\text{H}_2\text{SO}_4$</td>
<td>100:1 chromic acid and $\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>2) Anode</td>
<td>Insoluble anodes like Pb, Pb with upto 7% Sn or Sb</td>
<td>Insoluble anodes like Pb, Pb with upto 7% Sn or Sb</td>
</tr>
<tr>
<td>3) Cathode</td>
<td>Object to be plated</td>
<td>Object to be plated</td>
</tr>
<tr>
<td>4) $\text{pH}$</td>
<td>2-4</td>
<td>2-4</td>
</tr>
<tr>
<td>5) Temperature</td>
<td>45-55°C</td>
<td>43-66°C</td>
</tr>
<tr>
<td>6) Current density (mA/cm$^2$)</td>
<td>145-430 A/ft$^2$</td>
<td>280-580 A/ft$^2$</td>
</tr>
<tr>
<td>7) Current efficiency (%)</td>
<td>8-12</td>
<td>10-15</td>
</tr>
<tr>
<td>8) Properties</td>
<td>Provides durable and good decorative finish on article, Bright appearance, wear resistance, corrosion resistance etc</td>
<td>It provides high hardness, low co-efficient for friction, wear resistance, corrosion resistance etc</td>
</tr>
<tr>
<td>9) Application</td>
<td>Provides durable and good decorative finish on automobiles, surgical instruments etc…</td>
<td>Extensively used in industrial and engineering applications.</td>
</tr>
</tbody>
</table>

**Main reactions involved are:**

Formation of chromic acid by the reaction of chromium trioxide with water.

- $\text{CrO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CrO}_4 \rightarrow \text{CrO}_4^{2-} + 2\text{H}^+$
  
  (chromium trioxide) \hspace{1cm} (chromic acid)

Chromic acid in equilibrium with dichromic acid.

- $2\text{H}_2\text{CrO}_4 \rightarrow \text{H}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + \text{H}_2\text{O}$
  
  (dichromic acid)

Electrons supplied to the cathode, reduce the salt of chromium to metallic chromium.

- $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

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

- Thick coating of hard Cr helps in wear resistance, lubrication, etc. also hardness increases, high heat resistance, non sticking property, good corrosion resistance.
• In Cr plating Cr is not used as anode, since Cr metal passivate (reduces the chemical reactivity) in acid sulfate medium, also Cr anode on dissolution gives rise to Cr(III) ions leads to the formation of black Cr deposit.

• In plating bath, \( \text{SO}_4^{2-} \) ions from \( \text{H}_2\text{SO}_4 \) acts as catalyst. Cr is present in \( \text{Cr}^{6+} \) state as \( \text{CrO}_3 \) in bath solution. In presence of \( \text{SO}_4^{2-} \) ions \( \text{Cr}^{6+} \) is converted to \( \text{Cr}^{3+} \).

• \( \text{PbO}_2 \) coating on anode oxidize \( \text{Cr}^{3+} \) to \( \text{Cr}^{6+} \) and control the concentration of \( \text{Cr}^{3+} \) ions. In presence of large excess of \( \text{Cr}^{3+} \) ions, a black Cr deposit is obtained.

\[
2 \text{Cr}^{3+} + 3\text{O}_2 \rightarrow 2\text{CrO}_3 + 6\text{e}^-
\]

**ELECTROLESS PLATING:**

“It is a technique of depositing a metal from its salt solution on a catalytically active surface of the substrate by controlled reduction of metal ions using a suitable reducing agent without the use of electricity.”

The reducing agent converts the metal ions to metal which gets plated over the catalytic surface.

\[
\text{M}^{n+} + \text{reducing agent} \rightarrow \text{M} + \text{oxidized product}
\]

The driving force in this process is autocatalytic redox reaction on preheated catalytic surface. The main advantage of this method is irregular shapes can be plated uniformly.

**Advantages:**

1) No electrical power required.
2) Plating may also be obtained on insulator and semiconductor.
3) Better throwing power compared to electroplating.
4) Coatings have unique mechanical, chemical and magnetic feature.
5) No hydrogen gas liberates at cathode, this results in good deposit.
6) Levellers are not required.

**Disadvantages:**

1) Generates more waste than other plating techniques.
2) Deposit is contaminated with oxidized product.
3) Rate of deposition is slow.
**DIFFERENCE BETWEEN ELECTROPLATING AND ELECTROLESSPLATING:**

<table>
<thead>
<tr>
<th>Property</th>
<th>Electroplating</th>
<th>Electrolessplating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Source (driving force)</td>
<td>Electrical energy (current)</td>
<td>Autocatalytic redox reaction</td>
</tr>
<tr>
<td>2) Anode</td>
<td>Separate anode is used</td>
<td>Catalytic surface of substrate.</td>
</tr>
<tr>
<td>3) Cathode</td>
<td>Object to be plated (treated to remove surface impurities)</td>
<td>Object to be plated (treated to make surface catalytically active)</td>
</tr>
</tbody>
</table>
| 4) Reactions            | At anode: \( M \rightarrow M^{n+} + ne^- \)  
At cathode: \( M^{n+} + ne^- \rightarrow M \)  
\( M^{n+} + \) Reducing agent \( \rightarrow M + Oxidized \) product | |
| 5) Reducing agent       | Reduction is brought about by electrons. | Reduction is brought about by reducing agent. |
| 6) Applicability        | Applicable only to conductors            | Applicable to conductors, semiconductors and insulators |
| 7) Throwing power       | Not satisfactory in case of objects with irregular shape. | Satisfactory irrespective of shape. |

**Electroless plating of Nickel:**

Before electroless plating process, the surface is thoroughly cleaned. Then, electroless plating is done under following conditions.

Pretreatment: The article to be plated is degreased and etched by treatment with organic solvent followed by dil. H\(_2\)SO\(_4\).

Electroless nickel is deposited directly on metals without any treatment (activation) in presence of reducing agents. However, non-metallic materials like plastics, glass etc., are catalytically activated by dipping in Sncl\(_2\) containing Hcl at 25\(^0\)C followed by Pdcl\(_2\).

Sncl\(_2\) reduces palladium ions on the surface of the object to palladium which catalyze the deposition reaction.

Plating bath composition, conditions and reactions involved in electroless plating of nickel are given as follows:

<table>
<thead>
<tr>
<th>Plating bath solution:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal ion solution</td>
</tr>
</tbody>
</table>
Reducing agent | Sodium hypophosphite (NaH₂PO₂) 20g/l
---|---
Complexing agent | Sodium succinate 15g/l
Buffer (pH = 4.5) | Sodium acetate 10g/l
Temperature | 93°C
pH | 4.5

**Plating reactions**

Anode reaction: \( \text{H}_2\text{P}o_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{P}o_3^- + 2\text{H}^+ + 2\text{e}^- \)

Cathode reaction: \( \text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} \)

Overall reaction: \( \text{H}_2\text{P}o_2^- + \text{H}_2\text{O} + \text{Ni}^{2+} \rightarrow \text{H}_2\text{P}o_3^- + 2\text{H}^+ + \text{Ni} \)

Since, \( \text{H}^+ \) ions are produces during the reaction the pH decreases. To maintain the pH at 4.5, buffer salt sodium acetate is added during the reaction.

**Applications**

1. It is used to obtain a wear resistance, corrosion resistance surface.
2. Ni coating on aluminium improves the solderability.
3. In the automotive industry bright nickel can be found on bumpers, rims, exhaust pipes and trim etc
4. It is also used in connectors for electronics commonly found in automobiles and electronic gadgets.

**ELECTROLESS PLATING OF COPPER ON PCB (PRINTED CIRCUIT BOARD):**

An important application of electroless copper plating is manufacture of printed circuit boards (PCB). The technique used to manufacture PCB is subtractive method. The base metal (substrate) used in this method is insulator (plastic material).

Copper deposits spontaneously in presence of suitable reducing agent on metal, but insulators like plastic and glass are to be activated before subjecting to electroless plating. This is done by dipping in the solution containing stannous chloride \( \text{SnCl}_2 \) and \( \text{HCl} \) then followed by dipping in palladium chloride \( \text{PdCl}_2 \) solution.

\[ \text{SnCl}_2 + \text{PdCl}_2 \rightarrow \text{SnCl}_4 + \text{Pd} \]

On drying, a layer of Pd is formed on surface.
Article to be plated is degreased and catalytically activated. Plating bath composition, condition and reaction involved in electro less plating of copper bare given as follows;

**Bath composition:**
1) Coating solution: Copper sulphate solution (CuSO$_4$) 12 gL$^{-1}$
2) Reducing agent: Formaldehyde 8 gL$^{-1}$
3) Complexing agent: EDTA (ethylene diamine tetra acetic acid) 20 gL$^{-1}$
4) Buffer: NaOH 15 gL$^{-1}$ + Rochelle salt (double salt of potassium sodium tartarate) 14 gL$^{-1}$
5) pH: maintained at 11
6) Optimum temperature : 25ºC

**Reactions involved:**

\[
\text{Cathode } : \quad \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \\
\text{Anode } : \quad 2\text{HCHO} + 4\text{OH}^- \rightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2e^- \\
\]

**Overall reaction :**

\[
\text{Cu}^2+ + 2\text{HCHO} + 4\text{OH}^- \xrightarrow{\text{catalytic surface of article}} \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2
\]

In this method, particularly in double sided multilayered boards, in which plating through holes is required, and this is not possible by electroplating process.

**Plating process:**

- A plastic board is degreased and etched in acid. It is then activated in Sncl$_2$ solution containing HCl at 25ºC followed by dipping in palladium chloride.
- The surface is dried to get a layer of palladium catalyst.
- The activated board is dipped in the bath solution and the process is continued till a copper layer of 5 to 100 thickness is obtained.
- Selected areas are protected by a photo resist and the rest of copper plated is etched away so as to get required type of circuit track.
- Double sided copper plating is preferred since more number of components may be placed in a small space.
- The connection between the two sides of PCB is made by drilling holes, followed by electroless Cu plating through holes.