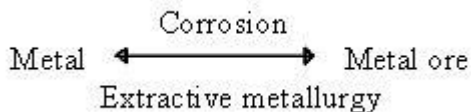


MODULE-2

CORROSION and METAL FINISHING

Defⁿ: Corrosion is a destruction reaction taking place spontaneously by chemical or electrochemical reaction of the metal by the surrounding environment on the surface of the metal.



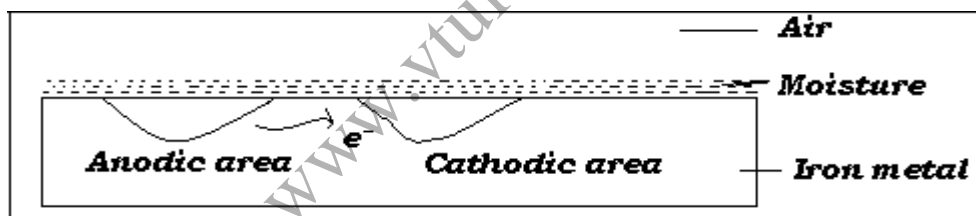
A slow and continuous process of destruction of a metallic substance through spontaneous chemical and electrochemical attack by its environment starting at its surface is called corrosion.

Reason: Pure isolated metals will have higher energy content than their corresponding ores and their compounds hence they have a natural tendency to revert back to combined form by combining with the contents of the environment such as gases, liquids, moisture etc. when exposed. This is the basic reason for corrosion.

Electrochemical theory of corrosion

According to electrochemical theory, corrosion of metals occurs due to the following changes, when they are exposed to the environment.

- 1) A large number of minute galvanic cells are formed which acts as anodic and cathodic areas.
- 2) At anode, the metal undergoes oxidation and electrons are liberated which migrates towards cathodic region
- 3) Oxygen of the atmosphere undergoes reduction at cathodic area in the presence of moisture forming hydroxyl ions at the cathode



Anodic reactions: At anode, the metal undergoes oxidation-liberating electrons



Ex: when iron is exposed to the environment it undergoes oxidation as



Cathodic reactions: The electrons released at anode migrate to the cathodic area and reduces oxygen to hydroxyl ions. The different cathodic reactions are,

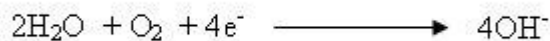
- a). In acidic medium: In acidic medium and in the absence of oxygen, hydrogen ions are reduced to hydrogen gas



b) In alkaline and in the absence of O₂. If the solution is alkaline and in the absence of oxygen the cathodic reaction is,



c) In neutral and aerated medium: when the solution is neutral and aerated, hydroxyl ions are formed as follows.



d) Formation of corrosion product: The hydroxyl ions migrate towards the anode and react with metal ions (Mⁿ⁺ ions) and forms corrosion product. In the case of iron OH⁻ reacts with Fe²⁺ ions and forms an insoluble hydrated ferric oxide known as brown rust.



If i_{corr} (corrosion current) is the current flowing,

Then Rate of corrosion = i_{corr}/nF grams per second. n=charge on the ions, F=Faraday constant

The total current due to the cathodic reaction ($\sum i_c$) must be equal but opposite in sign, to the total current flowing out due to the anodic reaction ($-\sum i_a$).

$$i_{\text{corr}} = -\sum i_a = \sum i_c$$

Galvanic Series: The arrangement of elements in the order of their standard reduction potential is referred to as emf or electrochemical series. Such an arrangement of few elements given in the table.

Mn ⁺ /Mn	E°(V)	Mn ⁺ /Mn	E°(V)
Li ⁺ /Li	-0.305	Sn ²⁺ /Sn	-0.14
K ⁺ /K	-2.93	Pb ²⁺ /Pb	-0.126
Ca ⁺ /Ca	-2.87	H ⁺ /H ₂	0.000
Na ⁺ /Na	-2.71	Cu ²⁺ /Cu	0.34
Zn ²⁺ /Zn	-0.76	Ag ⁺ /Ag	0.80
Fe ²⁺ /Fe	-0.44	Hg ²⁺ /Hg	0.85
Cd ²⁺ /Cd	-0.40	Pt ²⁺ /Pt	1.20
Ni ²⁺ /Ni	-0.236	Au ³⁺ /Au	1.38

1). A negative value indicates oxidation tendency and a positive value indicates reduction tendency with respect to hydrogen.

2).The metal with lower electrode potential is more reactive and as the electrode potential increases, the reactivity decreases and metals with higher electrode potentials are nobler.

3).Metals with lower electrode potentials have the tendency to replace metals with higher electrode potential from their solutions, for example, Zn displaces Cu, Cu displaces Ag.

4).Metals with negative electrode potentials can liberate hydrogen from acidic solutions.

Primary Factors (Related to metal)**1. Nature of the metal & its surface state:**

Corrosion is a surface phenomenon smaller the size more will be the area exposed & more will be the corrosion. The rough surface will suffer more corrosion compared to the smooth surface. Impure metal is more corrosive.

2. Nature of the corrosion product:

Corrosion of the metal the product is usually its oxide which forms a layer on its surface. The oxide layer determines the corrosion rate. If the corrosion product is adherent, insoluble, stable, uniform, nonporous with low ionic & electronic conductivities then the layer will form a barrier for further corrosion, hence prevents corrosion.

Secondary factor (Related to Environment)**1. pH of the medium:**

Acidic medium i.e. lower pH is more corrosive than the alkaline medium (i.e. higher pH) however some metals like Zn, Al etc. undergo corrosion in alkaline medium also hence a pH range around 7 i.e. (6-8) gives the least corrosion.

2. Temperature:

The rate of corrosion reaction always increase with temperature, higher temperature increases the rate of diffusion of ions, it also decreases the passivity of certain metals hence more corrosion is seen at elevated temperature.

3. Relative anodic & cathodic area:

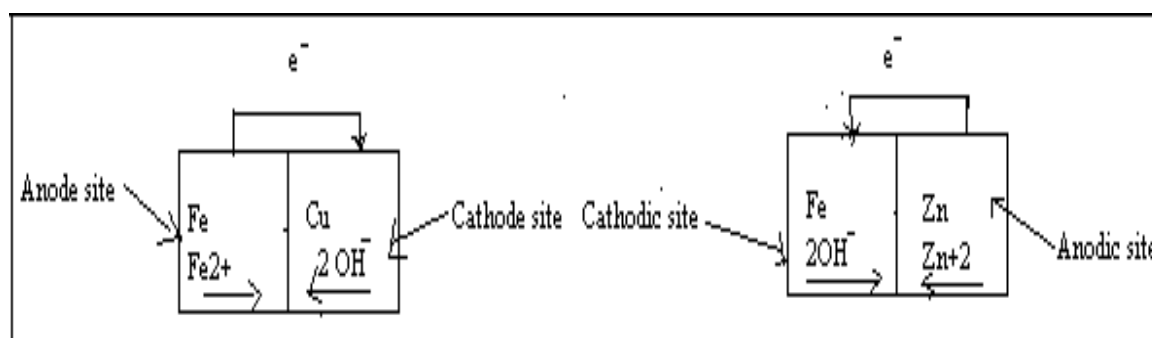
Larger the cathodic area and smaller the anodic area exposed more will be the corrosion of anodic metal & vice versa.

4. Conductivity of the corroding medium:

Higher the conductance more will be the flow of corrosion current, hence corrosion of metal buried in clay and mineralized soils will be more than those under dry sandy soils.

Types of Corrosion**1). Differential metal corrosion:**

When two dissimilar metals are in direct contact with one another and exposed to a corrosive conducting medium, the metal higher up in the electrochemical series behaves as an anode and suffers from corrosion, whereas the metal lower in the electrochemical series become cathode with respect to the other metal and is protected from corrosion. This type of corrosion is also known as **Galvanic corrosion**.



When Zn & Cu metals are electrically connected and exposed to an electrolyte, Zn metal higher in galvanic series forms the anode and suffers from corrosion whereas Cu lower in electrochemical series forms cathode hence protected from corrosion. The extent of corrosion depends on the difference in the electrode potential of the two metals and also their relative areas exposed if the potential difference between the electrodes is high,

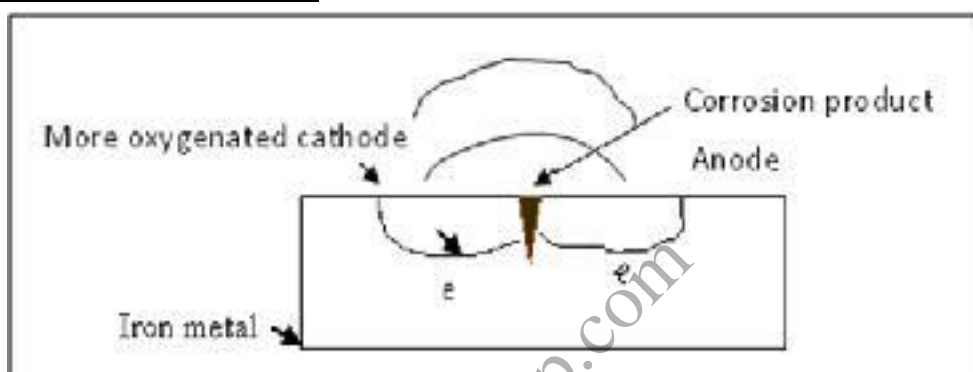
greater the extent of corrosion. **Eg:** 1). Brass taps fixed to an iron pipe. 2). Steel screws in a brass marine hardware.

2). Differential Aeration Corrosion:

When a metal surface is exposed to differential air or oxygen concentrations forms differential aeration cell. The more oxygenated part of the metal behaves as a cathode and the less oxygenated part become anode. Differential aeration of metal causes a flow of current called the differential current & the corrosion is called as differential aeration corrosion.

This phenomenon can be explained by two types of differential aeration corrosion. They are, **a. Pitting Corrosion** and **b. Water line corrosion**

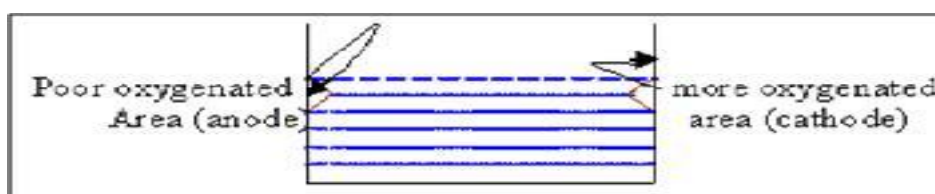
a. Pitting Corrosion:



- Pitting corrosion** is a localised accelerated attack in which only small areas of the metal surface are attacked whilst the remainder is largely unaffected. This localised attack results in pitting. The pits may initiate and propagate to a certain depth resulting in the formation of cavities and becomes inactive.
- Pitting is very destructive and frequently ruins the tubes, pipes etc.
- Pitting is due to breakdown or cracking of the protective film on a metal at specific points.
- The presence of impurities like sand, dust, scale, etc., on the surface of metal, leads to pitting.
- Pitting corrosion is due to the formation of differential aeration cell.
- This attack becomes more intensified with time.

b. Water line corrosion:

- Differential aeration accounts for the corrosion of metals partially immersed in a solution, just below the water line. This type of differential aeration corrosion is also known as **water line corrosion**.



- Consider a steel tank containing water. The maximum corrosion takes place along a line just beneath the level of water meniscus. The area above the waterline is highly oxygenated and acts as the cathodic and completely unaffected by corrosion. (Eg. Marine plants attacking themselves on the sides).

Corrosion control:

Corrosion can be controlled by preventing the formation of galvanic cells the common methods used to control corrosion of metals are as follows.

Anodizing:

Defⁿ: - 'A process in which a protective active oxide is formed chemically on metals is called anodization'.

Anodization of Al

Anodization of Al consists of the following steps.

Step 1: - Preparation of Al base metal surface.

- The metal surface is degreased using organic solvents & rust is removed by sand blasting, grinding, acid pickling etc.

Step 2: - Al base metal is placed in an oxidizing bath like chromic acid or boric acid, H₂SO₄

Step 3: - The base metal is made anode and connected to a battery while lead is used as cathode. A current of 150mA/Cm³ at 10-28v at 25-40°C is passed Al₂O₃ gets deposited. Then it is washed with water.

Step 4:- The base metal with the oxide layer is boiled with water using colouring agent to get desired colour.



Step 5:- The base metal is further treated with nickel acetate to increase its resistance to corrosion.

Application:

- It is used to make soapbox, Tiffin carriers, window frames etc.

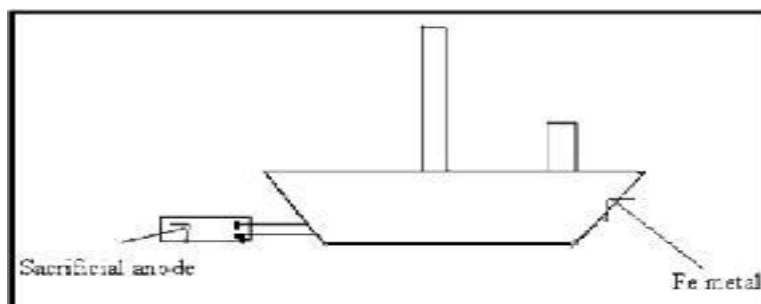
Cathodic protection:

The principle of this method is to convert the corrosive base metal into a cathode. This is done by

1. Sacrificial anodic protection.
2. Impressed current technique.

1. Sacrificial anode method:

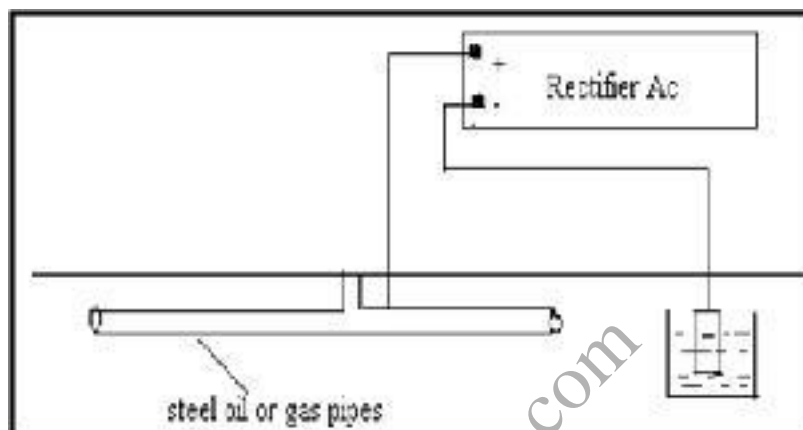
The metallic structure to be protected is made relatively a cathode by using another anodic metal contact with it. So that the corrosion is now concentrated on more anodic metal protecting the base metal from corrosion. The sacrificial anodes to be replaced by fresh ones as and when it is required. Commonly used sacrificial anodes are: Mg, Zn, Al etc.



This method is generally employed for the structures buried in water or streamers anchored in the sea, buried pipelines, ship hulls etc.

2. Impressed current technique:

In this method the anodic base metal which is oxidizable in corrosion reaction is supplied with electrons the current is applied in the opposite direction to nullify the corrosion current i.e. through a small current flow by means of a battery so that oxidation is suppressed and corrosion of the base metal is reduced. An insoluble anode (ex: graphite, high silicon content iron, etc.) is buried in the soil and connected to the structure to be protected. The anode is usually placed in a backfill, to provide a better electrical contact with the surroundings. This is employed to large metal structures buried in soil.



Metal coating:

Covering the metal (substrate or base metal) with a layer of another metal in order to control the corrosion of the base metal by the environment is called as a metal coating.

Galvanizing:

Coating of Zn on Fe is commonly called as galvanization. It is an anodic metal coating process; this is done using hot dipping method which involves several steps.

Step 1: Preparation of base metal surface.

- a. Cleaning with organic solvents likes trichloroethylene.
- b. Sandblasting to remove scale.
- c. Grinding and polishing to remove rust.
- d. Acid pickling to remove traces of oxide layer.
- e. Washing with water and drying.

Step 2: Hot dipping.

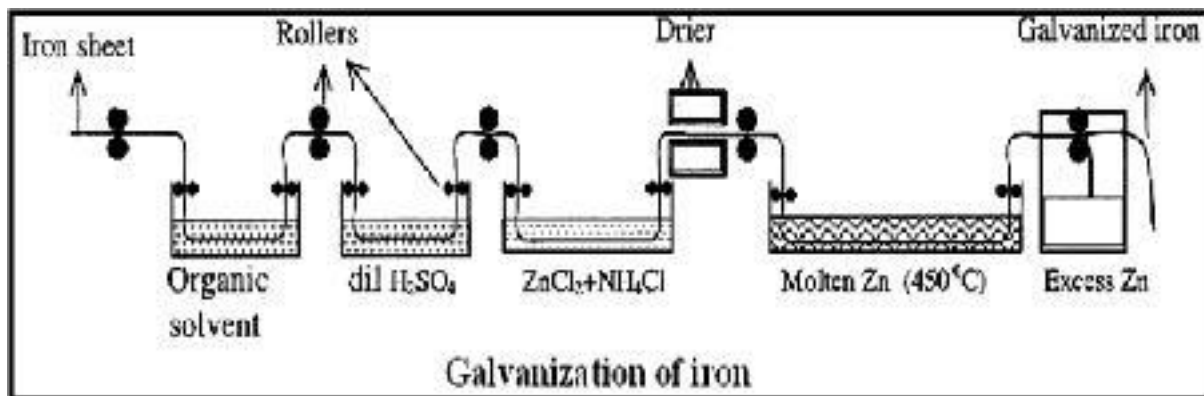
The base metal is dipped in molten Zn at 425-432^oC with ammonium chloride or ZnCl₂ as flux.

Step 3: Removal of the excess coating of Zn.

This is done by centrifuging in the case of a small article or by calendaring in the case of a sheet.

Step 4: Annealing

The substrate is heated above the melting point of Zn & cooled slowly.

**Advantages:**

Since the coating is anodic in nature the exposure of base metal will not cause corrosion.

Disadvantages:

Since Zn salts are poisonous food materials cannot be stored in container.

Uses:

To make galvanized articles.

In the making of roofing sheets, buckets, wires, pipes.

To manufacture automobile parts, bolts & nuts, nails etc.

METAL FINISHING:

Defⁿ: Metal finishing is the process of deposition of a layer of one metal on the surface of substrate (metal, plastic etc) or the process of conversion of a surface layer of atoms on a metal into an oxide film. (Note: Metal finishing is the process of surface modification of a metal)

Electroplating and Electroless plating are two important techniques of metal finishing.

Technological importance of metal finishing: Metal finishing is carried out to obtain technologically important surface properties. These properties are:

1. A decorative appearance.
2. An improved corrosion resistance.
3. An improved heat resistance.
4. An improved surface hardness. (An improved resistance to wear and tear. An improved resistance to abrasion.)
5. Improved solderability.
6. Good thermal conductivity.
7. Good electrical conductivity.
8. Good thermal reflectivity.
9. Good optical reflectivity.

Principles of Metal Finishing:

a) Polarization:

Defⁿ: - Polarization is defined as a process where there is a variation of electrode potential due to an inadequate supply of ionic species from the bulk of the solution to the electrode surface.

Consider an electrolytic cell under operation. When current is being passed, positive ions are produced at the anode and are consumed at the cathode. If the diffusion of ions in the electrolyte is slow, there will be an accumulation of positive ions in the vicinity of the anode. Similarly, there will be a depletion of ions in the vicinity of the cathode. Under these conditions, the anode and cathode are said to be polarized. This type of polarization is known as concentration polarization. (**Note: In galvanic cells, polarization leads to a variation of electrode potential.**)

In electrolytic cells, polarization leads to use of higher potentials than required theoretically.

Factors affecting the electrode polarization:

1. Nature of the electrode: Electrodes with rough surface have low polarization.
2. Nature of products formed at the electrode: If the products form a film on the surface, polarization increases.
3. Nature of the electrolyte: Lower the concentration of the electrolyte, lower is the polarization.
4. Temperature: Higher the temperature, lower is the polarization, because, at higher temperatures rate of diffusion of ions is higher.
5. The rate of stirring of the electrolyte: Stirring helps in minimizing the polarization effects.

b) Decomposition potential:

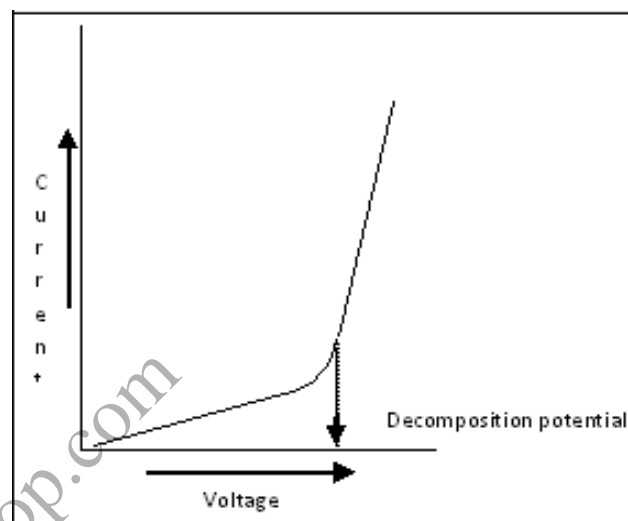
“When an electric current is passed through an electrolyte, electrolysis takes place only when applied voltage is above a certain value called a **decomposition Voltage**” below this value no electrolysis occurs since the current passing through the cell is very low. Consider the electrolysis of a dilute acid, only when the applied voltage exceeds 1.7 V there is an evolution of oxygen & hydrogen, below this value no electrolysis occurs.

The decomposition voltage may be defined as “**The minimum external voltage that must be applied in order to bring about continuous electrolysis of an electrolyte**” Electrolysis of the salt solution also occurs above a certain minimum voltage.

A plot of current v/s applied voltage is as shown in the figure

When the applied voltage is small the increase in current is very slight, however, beyond the decomposition potential there is a sharp increase in the current. The decomposition voltage of an electrolyte is due to emf of the cell set by the products of electrolysis. The product formed accumulate on the electrode and a cell is set up which exerts a back emf which resists the

flow of current until the applied voltage exceeds this emf. The magnitude of the back emf is same as the decomposition potential.



c) Over voltage (over potential) (η):

Defⁿ:- Over voltage is defined as the excess voltage that has to be applied above the theoretical decomposition potential to start the electrolysis.

$$\eta = \text{Experimental decomposition potential} - \text{Theoretical decomposition potential.}$$

Example: For electrolysis of water using smooth platinum electrodes, the theoretical decomposition potential is 1.23 V. The experimental decomposition potential is 1.7 V. The difference, 0.47 V, is the over voltage.

It was observed that during electrolysis back emf arises and a minimum voltage is to be applied for continuous electrolysis. If the back emf is overcome, electrolysis must proceed. This back emf may be calculated by considering the cell set up by the products of electrolysis and it is equal to the emf of the reversible cell at one atmosphere. When this emf is compared with the decomposition potential, it is found that the value is higher than the required emf value. **The difference between the observed voltage and the theoretical voltage is known as over voltage.** Over voltage depends on nature of electrode, the physical state of the substances deposited, current density and temperature. It is due to the surface phenomenon. It depends on how ions are discharged and the rate at which they are discharged. Hydrogen overvoltage is of particular significance in many electrolytic reactions and especially in electroplating and corrosion.

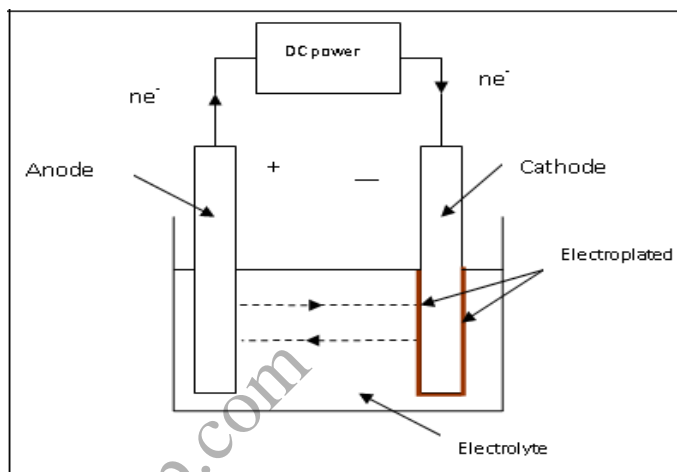
Electroplating:

Definition: Electroplating is the process of electrolytic deposition of a metal on the surface of another metal; the substrate may be another metal, a polymer, a ceramic or a composite.

Principal components of an electroplating process: The principal components are shown in the following figure.

The main components are:

1. Electroplating bath: It contains a suitable salt solution of the metal being plated. It also contains other additives.
2. Anode: It may be a rod or pellets of the metal being plated. It may be an inert electrode. It should be electrically conducting.
3. Cathode: It is the article to be plated. It should have an electrically conducting surface.
4. Inert vessel: It contains above mentioned materials. It may be a vessel made of rubber lined steel, plastic concrete or wood.



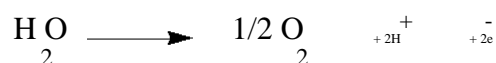
5. D.C. power supply: The positive terminal of the power supply is connected to the anode and the negative terminal is connected to the cathode.

Reactions at anode and cathode during electroplating:

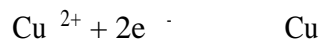
At anode oxidation takes place



When the anode used is an insoluble (inert) anode, oxygen evolution occurs at the anode:



At the cathode, reduction occurs. The metal gets deposited on the cathode surface. For example:



Surface preparation (Pretreatment):

The importance of surface preparation before electroplating: A good adherent deposit is obtained only if the substrate surface is free from dirt, grease, oxide scale and rust. Therefore it is necessary to clean the surface thoroughly before electrodeposition. If bright deposits are required, the surface must be smooth. Surface cleaning involves following steps:

1. Removal of organic substances – solvent cleaning, alkali cleaning.
2. Removal of inorganic substances – mechanical cleaning, pickling.
3. Rinsing with water

1. Removal of organic substances – degreasing process:

a) Organic solvent cleaning: It is used to remove oils, greases etc. from the surface. For cleaning, organic solvents such as trichloroethylene ($\text{CCl}_2 = \text{CHCl}$), methylene chloride (CH_2Cl_2), carbon tetrachloride (CCl_4) etc. are used.

In vapour phase degreasing method, vapours of the solvent (trichloroethylene) are allowed to condense on the metal surface. The condensed liquid washes away the oil, grease and other organic matter from the surface.

b) Alkali cleaning: Residual oil and grease from the surface are removed by treatment with alkaline solutions (NaOH , Na_2CO_3 etc.) Alkali cleaning is made more effective by making the metal cathodic in a hot alkali solution. The hydrogen gas liberated at the cathode helps to dislodge the greasy matter.

2. Removal of inorganic substances – descaling process:

a) Mechanical cleaning: It is used to remove oxide scales and rust from the metal surface. Simple mechanical cleaning involves hand cleaning using sand paper, bristle brush etc. Other methods involve polishing the surface i) using grinding wheels, ii) by sandblasting and iii) by electropolishing.

b) Pickling: It is used to remove oxide scales and rust present on the metal surface by dissolution. Pickling involves dipping the object in dilute acids (HCl , HNO_3 , H_2SO_4 or a mixture) for a considerable period of time.

Rinsing with water: The object is finally rinsed with deionized water.

Electroplating of chromium:-

The surface of the object is cleaned thoroughly. Organic substances are removed by solvent cleaning and alkali cleaning. Inorganic substances are removed by mechanical cleaning and pickling. Finally, the surface is washed with deionized water. Then, chromium plating is done under the following conditions.

1. Plating bath composition	Chromic acid (H_2CrO_4) + H_2SO_4 in the weight ratio 100 : 1
2. Operating temperature	45-60 °C
3. Current density	100 – 200 mA cm^{-2}
4. Current efficiency	8-12%
5. Anode	Insoluble anode: Pb-Sb or Pb-Sn alloy coated with PbO_2 .
6. Cathode	Object to be plated
7. Anodic reaction	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 \quad \begin{matrix} + \\ +2\text{H} \end{matrix} \quad \begin{matrix} - \\ +2\text{e} \end{matrix}$
8. Cathodic reaction	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$
9. Applications	1. Used in the decorative coating. 2. Used in corrosion resistant coating.

In chromic acid, chromium is present in 6+ oxidation state. It is first reduced to 3+ state by a complex anodic reaction in the presence of sulphate ions. The Cr^{3+} then gets reduced to Cr on the substrate surface. For a good deposit, the Cr^{3+} concentration must be low. The PbO_2 oxidizes a part of Cr^{3+} to Cr^{6+} , thus reducing the concentration of Cr^{3+} . In chromium plating, we do not use chromium metal as anode due to the following reasons.

1. If chromium dissolves at the anode, there will be a high concentration of Cr^{3+} in solution. In such cases, a black deposit is obtained.
2. In acidic solutions, chromium may undergo passivation.

ELECTROLESS PLATING:

Defⁿ:- Electroless plating is a method of depositing a metal over a substrate by controlled chemical reduction of metal ions by a suitable reducing agent **without** using electrical energy.

Metal ions + reducing agent \rightarrow Metal + oxidized product.

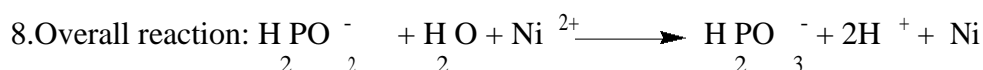
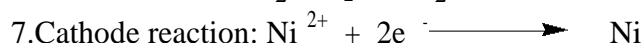
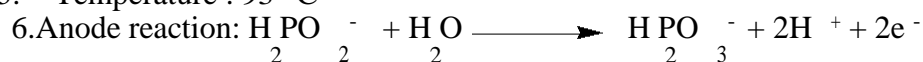
Advantages of electroless plating:

1. Electrical equipment is not required.
2. Semiconductors and insulators can also be plated.
3. Electroless plating baths have better throwing power.
4. Electroless coatings are harder than the electrodeposited coatings.
5. Electroless deposits possess' unique chemical, mechanical & magnetic properties.

Electroless plating of Ni :-

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

1. Plating bath solution : NiCl_2
2. Reducing agent : Sodium hypophosphite.
3. Complexing agent & exaltant : Sodium succinate.
4. Buffer ($\text{p}^{\text{H}} = 4.5$) : Sodium acetate.
5. Temperature : 93°C



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

Applications:

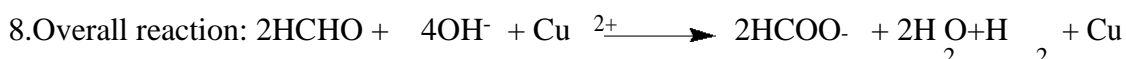
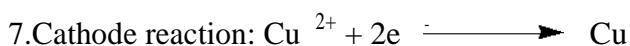
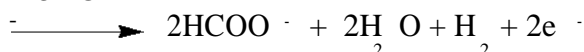
1. Used to obtain a wear resistant surface.
2. Ni coating on aluminum improves the solderability.
3. Ni coating on polymers is used to obtain decorative knobs in hi-fi equipment, tops on bottles etc.

Electroless plating of Copper (PCB- Printed Circuit Board):

Before electroless plating, the surface is cleaned thoroughly. Insulators such as plastics and printed circuit boards are activated by dipping first in stannous chloride (SnCl₂) and then in palladium chloride (PdCl₂). Then, the electroless plating is done under the following conditions:

1. Plating bath solution : CuSO₄
2. Reducing agent : Formaldehyde (HCHO)
3. Complexing agent and exultant : EDTA
4. Buffer (pH = 11) : Sodium hydroxide and Rochelle salt (Na-K-tartrate)
5. Temperature : 25 °C

6. Anode reaction: 2HCHO + 4OH⁻



Formaldehyde and copper sulphate are added to the plating bath periodically.

Applications:

1. Widely used for moralizing (PCB's) printed circuit boards.
2. For producing through hole connections.
3. For plating on non-conductors.
4. As an undercoat for electroplating.
5. For decorative plating on plastics.

Distinction between electroplating and electroless plating:

Property	Electroplating	Electroless plating
Source	Electrical energy is obtained from an external source.	No electrical energy is required
The site of anodic reaction.	The anodic reaction takes place at separate anode used in the electrolytic cell.	The site of anode reaction is the article to be plated.
The site of cathodic reaction.	Article to be plated acts as cathode	Catalytic surface on the article to be plated
Anode	Metal	Reducing agent in solution
Type of deposit obtained	Pure	Contaminated
Type of cathode used for plating	Plating is carried out on metals.	Plating may be carried out on insulators (ex: plastics) and semiconductors.
Anode reaction	$M \longrightarrow M^{n+} + ne^-$ $H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$	Reducing agent \rightarrow Oxidized product + n e ⁻
Cathode reaction	$M^{n+} + ne^- \longrightarrow M$	$M^{n+} + ne^- \longrightarrow M$

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