Corrosion is defined as the **"destruction or deterioration of a metal or its alloy and consequent loss of metal, caused due to direct chemical action or electrochemical reactions with its environment".**
Several metals undergo corrosion when exposed to air, water or other substances.
The primary factors which initiate corrosion of metals **are atmospheric air and water**
Corrosion of metals can be regarded as the reversal of its extraction.
Example: Rusting of Iron

Corrosion may occur either in a dry environment or in an aqueous medium. The former is called dry corrosion and the latter is wet corrosion.

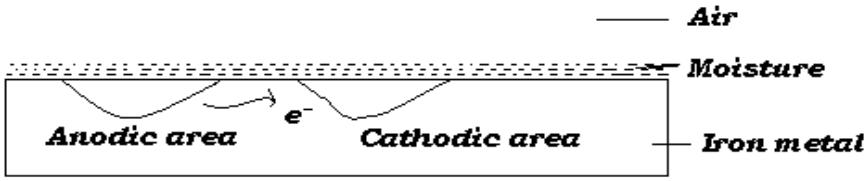
Dry Corrosion: Dry corrosion occurs in the absence of moisture or conducting electrolyte medium, due to direct attack of metals by dry gases mainly through chemical reactions. Ex: the attack of dry gases such as O_2, Halogen, H_2S, SO_2, NO_X etc., on a metal to form an oxide layer over the surface. However, such a process is not common.

Wet Corrosion: Wet corrosion involves reactions in aqueous medium. The conducting surface of the metal undergoes an electrochemical reaction with the moisture & oxygen present in the atmosphere. Ex: Rusting of Iron. Wet corrosion can be better explained on the basis of electrochemical theory.

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

$$\underset{\text{Metal}}{M} \longrightarrow \underset{\text{Metal ions}}{M^{n+}} + ne^-$$

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

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

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.

$$2H^+ + 2e^- \longrightarrow H_2$$

b) In alkaline and in the absence of O_2. If the solution is alkaline and in the absence of oxygen the cathodic reaction is,

$$2\,H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

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

$$2\,H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

d) Formation of corrosion product:

The hydroxyl ions migrate towards anode and react with metal ions (M^{n+} ions) and forms corrosion product. In the case of iron OH- reacts with Fe^{2+} ions and forms an insoluble hydrated ferric oxide known as brown rust.

$$2Fe^{++} + 4OH^- \longrightarrow 2Fe(OH)_2$$

$$2Fe(OH)_2 + O_2 + (n-2)\,H_2O \longrightarrow (Fe_2O_3 . nH_2O)\ \text{Rust}$$

Factors Affecting the Rate of Corrosion:-

The important factors, which affect on the rate of corrosion, are

I. Nature of the metal: (Electrode Potential)

The Metal undergo corrosion is dependent on the nature of the metal. The metals with **lower electrode potential** values are more reactive than the metals with **higher electrode potential** values. The more reactive metals are more susceptible for corrosion.

Example: The active metals like K, Na, Mg, Zn etc with low Electrode potential values are highly susceptible for corrosion. The nobel metals such as Silver, gold, Platinum etc., with higher electrode potential values are less susceptible for corrosion.

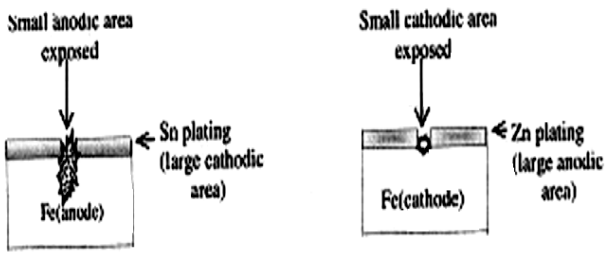
Exceptions: Metals and alloys which show passivity are exceptions for this general trend. Such metals form a protective coating on the surface which prevents corrosion.

II. Nature of corrosion product:

If the nature of corrosion product is **adherent, insoluble, stable, non volatile and non-porous, with low ionic and electronic conductivity**, then it acts as a protective film which prevents further corrosion. The film acts as a barrier between the fresh metal surface and the corrosive environment. On the other hand, if the nature of corrosion product is **non-adherent, soluble, unstable, conducting and porous**, then the corrosion process continues even after the formation of corrosion product.

Example: In oxidizing environment metals like **Al, Cr, Ti** etc. forms protective metal oxide films on their surfaces which prevent further corrosion. Stainless steel forms a protective film of Cr_2O_3 on the surface. Metals like Zn, Fe, Cd, Mg ,etc .do not form protective layer and are readily under goes corrosion .Therefore the rate of corrosion depends on the nature of corrosion product.

III. Ratio of Anodic to Cathodic Areas:



Rapid corrosion at small anodic area

Slow corrosion at the small exposed area of Fe

Corrosion of iron at anodic and cathodic areas

If a metal has small anodic and large cathodic area the rate of corrosion increases and vice versa. This is because when anode is small the electrons liberated during oxidation are completely consumed on large cathodic surface for the reduction reactions and rate of corrosion increases.

Example: If an iron sheet coated with tin has small pin holes, a small anode and a large cathode areas will form, which results in intense localized corrosion. If zinc plating on iron peels off at some points, the rate of corrosion of iron is low due to formation of large anodic and small cathodic areas.

IV. Nature of medium

- **Temperature**: Increases in temperature results in an increase in the conductance of the aqueous medium and rate of corrosion also increases and vice versa.
- **p^H**: Rate of corrosion increases with decrease in pH.
  - If pH>10, the rate of corrosion ceases due to the formation of protective coating of hydrous oxides on the metal.
  - If pH is between 3-10, the rate of corrosion depends upon the presence of oxygen on the Cathodic area for reduction. Higher the concentration of O_2, higher the rate of corrosion.
  - If pH<3 rate of corrosion is high even in the absence of air due to evolution of hydrogen at the cathodic region.
- **Conductivity**:

  Rate of corrosion increases with increase in conductance of medium.

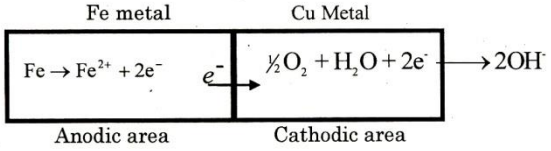
  For example, rate of corrosion of metal will be higher in wet atmosphere than dry atmosphere due to more conductance. Similarly metal undergo rapid corrosion in ocean water than in river water.

Types of corrosion:

Differential metal corrosion:

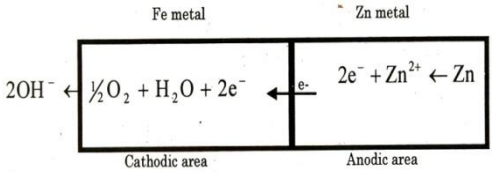
It occurs When two dissimilar metals are in .contact with each other, the metal with lower electrode potential becomes anodic and undergoes corrosion, whereas, the metal with higher potential becomes cathodic and remains unaffected. The rate of corrosion depends mainly on the difference in potential between two metals. Higher the difference, faster is the rate of corrosion.

Example:- a) Standard electrode potential of Fe (-0.44 V) is less than that of Cu (0.34 V). Therefore, when iron is in contact with copper, iron becomes anodic and undergoes corrosion, whereas copper becomes cathodic and remains unaffected



Differential metal corrosion

b) Standard electrode. potential of Zn (-0.76 V) is less than that of Fe (-0.44 V). Therefore, when iron is in contact with zinc, Zn becomes anodic and undergoes corrosion. Fe becomes cathodic and remains unaffected.



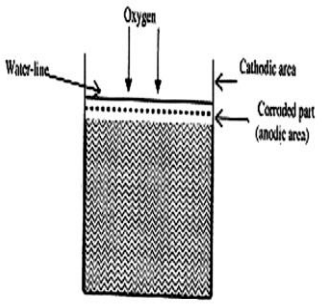
Differential metal corrosion

Differential aeration corrosion-

This type of corrosion occurs when a metal is exposed to different concentrations of Oxygen. The part of metal which is more exposed to air act as cathode and remains unaffected. The other part of the metal, which is less exposed to air act as anode and undergoes corrosion.

i) **Water line corrosion:**

It is differential aeration type of corrosion observed in water storage tanks, ships, etc



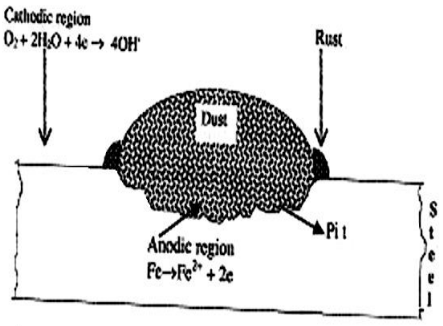
Water-line corrosion

During water line corrosion, the part of the Metal below waterline is exposed to less Oxygen concentration act as anode and undergoes corrosion than the other part which is more exposed to atmospheric oxygen which acts as cathode.

At anode $Fe \longrightarrow Fe^{++} + 2e^-$

At cathode $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

ii) **Pitting corrosion:** This is an example of differential aeration corrosion.



Pitting corrosion

Pitting corrosion occurs when small particles like dust, mud etc get deposited on metals surface. The portion of metal covered by the dust or other particles is less aerated and acts as anode. The other portion of the metal exposed to more oxygen of the environment act as cathodic region. Corrosion takes place at the portion below dust and a small pit is formed. Then the rate of corrosion increases due to small anodic area and large cathodic area.

At anode $Fe \longrightarrow Fe^{++} + 2e^-$

At cathode $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

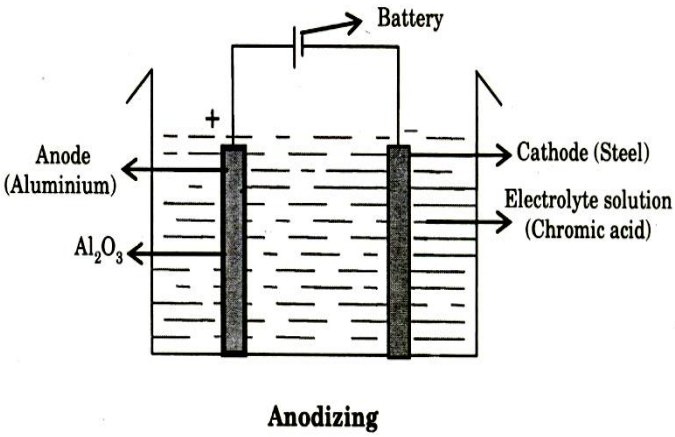
Corrosion control:-

INORGANIC COATINGS:

Inorganic coatings are surface conversion coatings or chemical conversion coatings. In this method outer surface of the base metal is converted in to protective coating through chemical reactions.
Example: Anodizing ,Phosphating.

ANODIZING: Anodizing is a process of artificially forming protective passive oxide film on the surface of metals such as Al, Mg, Ti, Zr, Ta, Cr, etc by electrochemical oxidation.

ANODIZING OF ALUMINUM:



In anodizing of aluminum, it is cleaned, degreased and polished and taken as anode in an electrolytic cell. It is immersed in an electrolyte consisting of 5-10% chromic acid. Steel or copper is taken as cathode. Temperature of the bath is maintained at 35°C. A current density of 100 Acm^{-2} or more is applied which oxidizes outer layer of Al to Al_2O_3 that gets deposited over the metal. **The passivity of aluminium is due to the formation of a thin and compact layer of aluminium oxide over the metal.** This phenomenon is known as anodizing or anodic oxidation or anodic passivity.

Uses: Anodized articles are used as an attractive, highly durable, corrosion resistant material in ceilings, floor, escalators, lobbies, staircase, curtain walls, , Tiffin carriers, soapboxes, household utensils, window frames, exterior for roofs, walls, buildings and in many home appliances.

METAL COATINGS:-

Deposition of protective metal over the surface of base metal is known as metallic coatings.

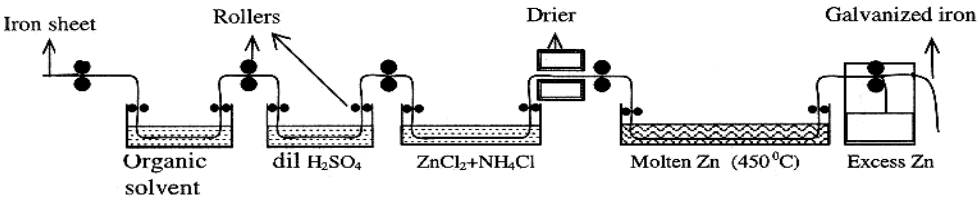
It is divided into anodic metal coatings and cathodic metal coatings.

a) **Anodic metal coatings**:

Anodic metal coatings are coatings which are anodic to the base metals. Examples are aluminium, magnesium, zinc, and cadmium coatings on iron. These metals are above iron in the galvanic series and undergo corrosion thereby protecting iron. A characteristic feature of anodic coatings is that the base metal on which the coating is done will not get corroded even if the coating peals off. This is due to the formation of large anodic and small cathodic areas.
Example: Galvanizing.

Galvanizing (Zinc coating on iron):

The process of coating a layer of zinc on iron by hot dipping is called as galvanizing. It involves the following steps,



Galvanization of iron

1) Iron sheet is passed through organic solvent to remove oil or grease present on it.
2) Then it is washed with dil.H_2S0_4 (pickling) to remove any rust (oxide layer) present on the surface '
3) Then it is treated with a mixture of aqueous solution of zinc chloride ($ZnC1_2$) and ammonium chloride (NH_4Cl) which acts as flux and then dried.

4) The treated sheet is dried and dipped in molten zinc at 430-470 ºC.
5) Excess zinc present on iron sheet is removed by rolling, wiping or passing blast of air.

Uses: Galvanization is used for roofing sheets, buckets, bolts, nuts, nails, pipes etc.

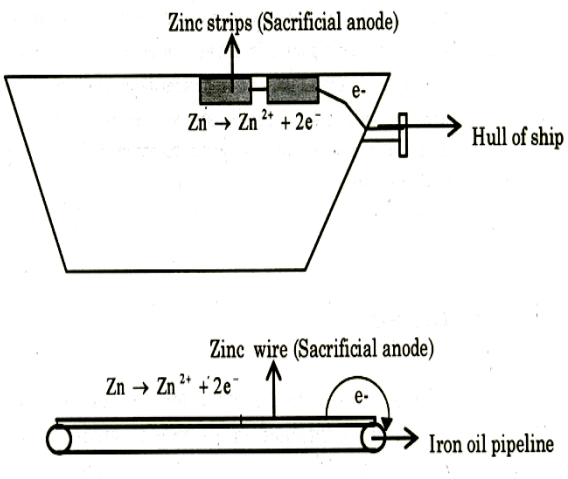
Galvanizing and tinning by hot dipping is more economical than electroplating. Hot dipping is limited to the coating of low melting point metals like Zn, Sn and Al over iron.

CATHODIC PROTECTION:-

Cathodic protection is a method in which the base metal to be protected from corrosion is made to act as cathodic by attaching more active anodic metal to it. The active anodic metal undergoes corrosion and base metal is protected from corrosion.

The following methods are used to protect metal from corrosion.
Example: a) **Sacrificial anodic protection method** **b) Impressed voltage method**

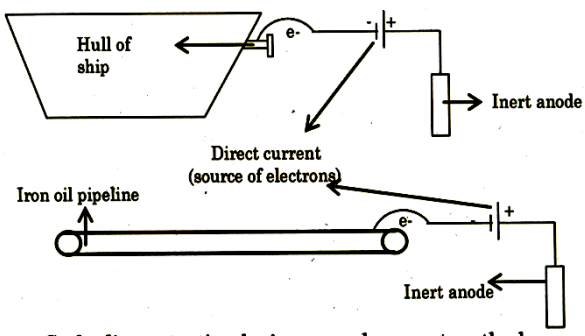
a) **Sacrificial anodic protection method-**



Cathodic protection by sacrificial anode method

In this method, metallic material to be protected is connected to a more active metal (anodic metal). Anodic metals like Zn or Mg can be employed to protect iron articles. When an anodic metal is in contact with iron specimen; a galvanic cell is set up, where anodic metal becomes anodic area and whole iron article becomes cathodic area. Anodic metal undergoes oxidation and provides electrons to the specimen. Hence the entire specimen becomes cathodic and thus protected from corrosion. In the process, anodic metal undergoes corrosion and sacrifices itself to protect the specimen; therefore it is called as sacrificial anode. Sacrificial anodes have to be replaced in due course of time.

b) **Impressed voltage method:**



Cathodic protection by impressed current method

In this method, the electrons are supplied from a source of direct current (**dc**). Metal structure to be protected is connected to negative terminal of a **dc** source. The positive terminal of **dc** source is connected to inert anode like graphite to complete the circuit. Potential greater than potential of anodic reaction is applied in the reverse direction to prevent anodic reaction. Thus, whole metal becomes cathodic and hence protected from corrosion.

METAL FINISHING

What is metal finishing? Mention the Technological importance of metal finishing.

It is a process of **modifying the surface properties** of a metal by deposition of a layer of another metal, a polymer or by the formation of an oxide film.

Technological importance of metal finishing:-

1. Imparting the metal surface to **higher corrosion resistance**.
2. Imparting improved wear and abrasion resistance.
3. Providing electrical and thermal conducting surface.
4. Imparting thermal resistance and resistance to impact.
5. Providing optical and thermal reflectivity.
6. In the manufacture of **electrical and electronic components** such as PCB's, capacitors and contacts
7. In electro framing of articles, electrochemical machining, polishing and etching.
8. To increase the **decorativeness** of metal surface.
9. In electrotyping and to build up material or restoration.
10. To improve solderability.

Electroplating:

The deposition of a metal, by electrolysis, over the surface of a substrate. The Substrate may be a metal, polymer, ceramic or a composite.

Principles governing electroplating:

The fundamental principles governing electroplating are

1. Polarization 2. Decomposition potential 3. Overvoltage

1. Polarization: (Polarization is an electrode Phenomenon)

During electrolysis, metal ions present at the vicinity (the area near) of cathode get reduced to metal atoms. Therefore concentration of metal ions at the vicinity of cathode decreases. To maintain the same concentration, metal ions must be supplied from the bulk of the solution to vicinity of the electrode. If metal ions are not supplied sufficiently, then the concentration of metal ions at the electrode surface decreases. This leads to decrease in the potential of electrode according to Nernst equation.

$$E = E^{O} + \frac{2.303RT}{nF} \log_{10} [M^{n+}]$$

This decrease in electrode potential due to insufficient supply of ions from bulk of the solution to surface of the electrode is called as polarization. Polarization occurs at anode also. Potential required to overcome polarization of anode and cathode is called as polarization potential.

Polarization of the electrode depends upon

1) Nature and physical state of the metal electrodes
2) Electrolyte concentration and its Conductivity.
3) Temperature
4) Products formed at the electrodes
5) Rate of stirring of the electrolyte

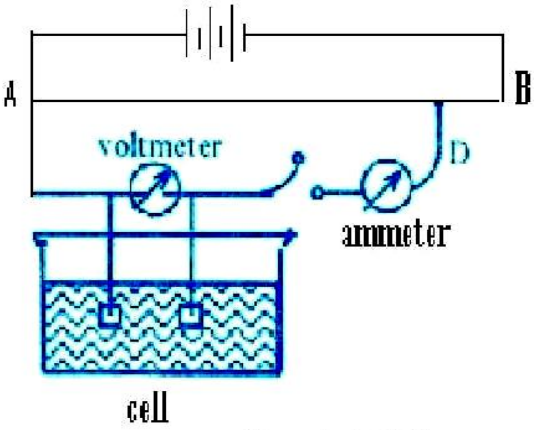
2. Decomposition potential:

The minimum external voltage that must be applied in order to carryout continuous electrolysis of an electrolyte in an electrolytic cell is called as decomposition potential (E_D).

Decomposition potential (E_D) is given by equation;

$$E_D = E_{Back} + \eta$$

Decomposition potential can be determined using an electrolytic cell as shown in figure.

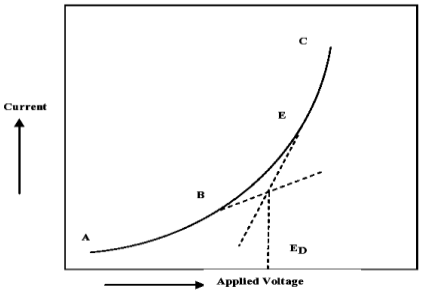


Electrolytic Cell

Generally an electrolytic cell consists of a single electrolyte into which a pair of electrodes is dipped. For example, in the electrolysis of water, a **pair of platinum electrodes** is immersed in a solution of an **acid or base**. It is found experimentally that a potential of about **1. 7 V** must be applied to the cell before there sets in a continuous evolution of hydrogen and oxygen. When a potential of less than 1.7 V is applied, the observation is a **momentary surge** of current which rapidly falls to zero. The reason for this is that, due to the initial passage of current, small amounts of hydrogen and oxygen are liberated at the cathode and the anode respectively. These gases are **adsorbed** on the cathode and the anode respectively and the inert platinum electrodes are converted into active hydrogen and oxygen gas **Electrolytic Cell** electrodes. The secondary cell formed produces a back emf opposing the applied emf. At potentials below 1.7 V, the back emf nullifies the effect of applied potential, and Continuous electrolysis takes place only when the applied emf is Sufficient enough to overcome the back emf.

$$E_{Back} = E_{cathode} - E_{anode}$$

Since, even inert electrodes are converted into active electrodes on electrolysis, and produce a **back emf**, it is necessary to apply a minimum required potential to produce continuous electrolysis of an electrolyte.



The decomposition voltage is obtained by extrapolation of the curve as shown in the diagram.

3. **<u>Overvoltage</u>:-**

Continuous electrolysis takes place when the applied voltage is slightly more than the decomposition potential (E_D). In a few cases, the applied voltage has to exceed the theoretical value by at least 1V for continuous electrolysis. This is known as overvoltage or over potential, represented by η.

Overvoltage is defined as the excess voltage that has to be applied above the theoretical decomposition potential for continuous electrolysis.

η = experimental decomposition potential - theoretical decomposition potential

i.e. $\eta = E_D - E_{Back}$

Overvoltage depends on several factors such as

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

Electroplating of chromium (hard and decorative)

Pre- treatment and Surface preparation of object.

Plating Bath Condition	**For Decorative Chrome Plating**	**For Hard Chrome Plating**
Chromic acid Bath	Chromic acid (CrO_3) and H_2SO_4 in 100:1 proportion	Chromic acid (CrO_3) and H_2SO_4 in 100:1 proportion
Temperature	45-55 ºC	43-66 ºC
Current density	100-200 mA/cm^2	215-430 mA/cm^2
Current Efficiency	8-12%	10-15%
pH	2-4	2-4
Anode	Insoluble Anodes: Pb-Sb or Pb-Sn alloy coated with thin layer of PbO_2	Insoluble Anodes: Pb-Sb or Pb-Sn alloy coated with thin layer of PbO_2
Cathode	Object to be Plated (pretreated)	Object to be Plated (pretreated)

Applications:

1. **Applications of Decorative Chrome Plating**
   These coatings are used to impart bright and decorative look to materials like automotive bumps, wheel rims, taps, handles etc.,
2. **Applications of Hard Chrome Plating**
   These coatings are used mainly to impart surface hardness and wear resistance to materials like in cutting edges of milling and drilling tools, hand guns, aircraft landing parts, axels, cylinder linings, piston rings etc.,

ELECTROLESS PLATING

Electroless plating is the deposition of a metal without the use of electrical energy.

It is defined as the controlled deposition of a continuous film of a metal from its salt solution on to a catalytically active surface with a suitable reducing agent without using electrical energy.

$$M^{n+} + \text{Reducing Agent} \xrightarrow{\text{Catalytically active surface}} M \rightarrow \text{Oxidized Product}$$

The driving force in electroless plating is an **autocatalytic redox reaction** on a pretreated active surface.

Advantages

(i) Use of **electrical power** and electrical contacts are **eliminated**.
(ii) **Semiconductors and insulators** like plastics can be plated.
(iii)Electroless baths have **better throwing power**. Intricate parts with irregular shapes, inside parts of tubes, recesses can be uniformly coated.
(iv) **Hydrogen gas** liberated is **not trapped** in blind holes.
(v) Electroless coatings are **harder**.
(vi) **No levelers** are required.
(vii) Deposits have **unique** chemical, mechanical and magnetic properties.

Principal components/Composition of an electroless plating bath: An electroless plating bath contains the following components:

1. A source of electro active metal in the form of a soluble salt. e.g. $NiCl_2$, $CuSO_4$
2. Reducing agent to reduce metal ions into metal atoms. e.g. Sodium hypophosphite, formaldehyde.
3. Complexing agents to form complex compounds with metal ions.
4. Exaltant (accelerator) to increase the rate of plating.
5. 5. Stabilizer to give more stability to solution.
6. 6. Addition agents such as brighteners.
7. 7. Buffer to control p^H.

ELECTROLESS PLATING OF NICKEL

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

Plating bath solution	$NiCl_2$ (20g/dm^3
Reducing agent	Sodium hypophosphite NaH_2PO_2. (20g/dm^3)
Complexing agent &exaltant	Sodium succinate. (15g/dm^3)
Buffer (p^H = 4.5)	Sodium acetate. (10g/dm^3)
Temperature	93 ^oC
Anode reaction	$H_2PO^-_2 + H_2O \rightarrow H_2PO^-_3 + 2H^+ + 2e^-$
Cathode reaction	$Ni^{2+} + 2e^- \rightarrow Ni$
Overall reaction	$H_2PO^-_2 + H_2O + Ni^{2+} \rightarrow H_2PO^-_3 + 2H^+ + Ni$

(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.)

<u>Applications</u>:

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.

<u>ELECTROLESS PLATING OF COPPER</u>

Pretreatment and Activation of the Surface:

The plastic board is degreased and etched in acid. It is activated by dipping in stannous chloride ($SnCl_2$) solution containing HCl at 25°C followed by dipping in palladium chloride ($PdCl_2$). The surface is dried to get a layer of palladium. Then, the electroless plating is done under the following conditions:

Coating solution	$CuSO_4$ solution (30g/ dm^3)
Reducing agent:	Formaldehyde 37% solution 170 mL/dm^3
Buffer:	NaOH (15g/L) + Rochelle salt (14g/L) (added to Control pH)
Complexing agent & exaltant	EDTA (17 g/L) -Improves the **quality** of plating & Exaltant (20g/L)-added to increase **rate** of plating
P^H	11
Temperature	25 ^oC
Anode reaction	$2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$
Cathode reaction	$Cu^{2+} + 2e^- \longrightarrow Cu$
Overall reaction	$Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu + 2HCOO^- + 2H_2O + H_2$

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

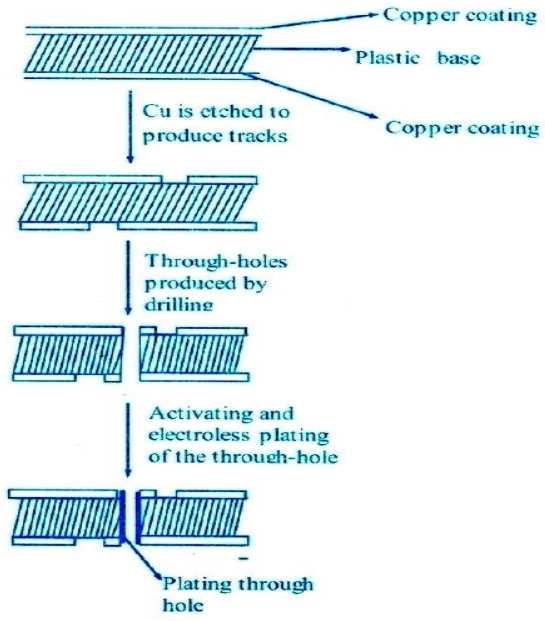
Applications: 1. Used for metalizing printed circuit boards.
2. Used to produce through-hole connections.

Applications:

Electroless Plating of Copper (Through hole connection in Printed Circuit Board-(PCB):

Plating Process

Base object used is a plastic board which is degreased and etched in acid. Then it is treated with $SnCl_2$ containing HCl followed by $PdCl_2$ to **activate** the surface. The activated board is then **immersed** in plating bath solution maintained at 25°C. Plating is carried out at a **rate** of 1 - 5 µm/h, till 5 - 100 µm thickness is obtained. Selected areas are protected and the rest of the Cu is etched away to produce the circuit pattern. The **connection** between both sides of track is made by **drilling hole** followed by **plating-through-holes** by electroless plating. Double sided PCB's are commonly used because of' **feasibility of packing** of more components in smaller space.



Various steps involved in electroless plating of copper on Double Sided Printed Circuit Board (PCB)

APPLICATIONS:

→ Widely used for moralizing (PCB's) printed circuit boards.

→ For producing through hole connections.

→ For plating on non-conductors.

→ As an undercoat for electroplating.

→ For decorative plating on plastics.

Distinction between Electroplating and Electroless plating:

	Electroplating	Electroless plating
Driving Force	Current	**autocatalytic redox reaction**
Anode	Separate anode	Catalytic surface of substrate
Cathode	Object to be Plated (treated to remove surface impurities)	Object to be Plated (treated to make surface catalytically active)
Reducing agent	Electrons	Chemical reagents (formaldehyde)
Applicability	Only to conductors	Conductors, semiconductors and insulators (Plastic)
Throwing Power	Plating baths don't have excellent throwing power	Plating baths have excellent throwing power
Levelers	Requires levelers	Does not require levelers
Reactions	$M \rightarrow M^{n+} + ne^-$ $M^{n+} + ne^- \rightarrow M$	M^{n+} + Reducing Agent $\longrightarrow$ M + Oxidized Product

**********ALL THE BEST**********