

CORROSION

Corrosion of Metals:

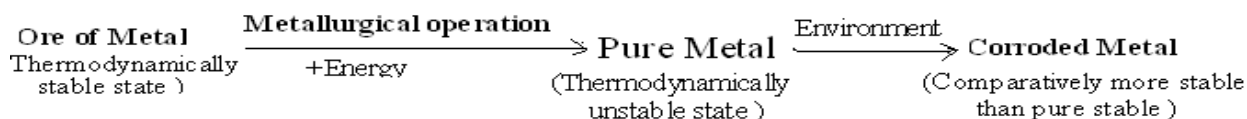
Corrosion is a process of gradual deterioration or destruction of metals or alloys from its surface due to unwanted chemical or electrochemical interaction of metal with its environment.

Examples:

1. Formation of a layer of reddish brown scale of hydrated ferric oxide on the surface of iron.
2. Formation of a green film of basic carbonate $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$ on the surface of Copper.

Cause of Corrosion:

The chemically combined state of metal, ore, possess low energy and is thermodynamically more stable state for metal. Pure metal is isolated from its ore by supplying considerable amount of energy. Isolated metal is said to be in excited state, possess high energy and thus thermodynamically unstable. Thus it is natural tendency of a metal to go back to its thermodynamically stable state. Metals do this by interacting with its environment to form surface compound and thus undergo corrosion.



Effects of Corrosion:

- (a) Due to corrosion, properties of metals such as malleability, ductility and electrical conductivity are lost.
- (b) Due to corrosion efficiency of metal is reduced.
- (c) Contamination of product will also take place if the corroded equipment is used.
- (d) The replacement of corroded equipment is time consuming; maintenance cost increases.

Types of corrosion

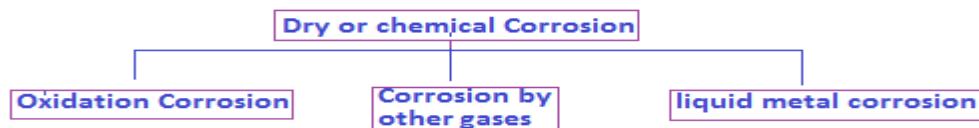
1. Dry or chemical Corrosion
2. Wet or Electrochemical of corrosion

1. Dry or chemical Corrosion

Dry corrosion occurs under dry conditions. This type of corrosion occurs mainly due to direct

chemical action of atmospheric gases such O_2 , Cl_2 , CO_2 , sulphur dioxide, NO_x , nitrogen or

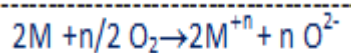
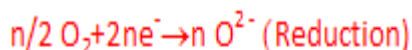
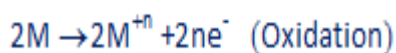
anhydrous inorganic liquid on the metal surface.



i. Oxidation corrosion (corrosion by oxygen):

Direct attack on metals by oxygen at ambient temperature in the absence of moisture leads to oxidation corrosion. Alkali and alkaline earth metals undergo corrosion even at ordinary temperatures whereas at high temperatures all metals except Ag, Au and Platinum are oxidized.

Mechanism:



Nature of the metal oxide (corrosion product) formed on the surface of the metal influences further rate of corrosion

- 1) **If metal oxide formed is stable, it protects underlying metal from further attack. Oxides of Pb, Al and Sn, hence inhibit further corrosion.**
- 2) If the metal oxide formed is unstable, it decomposes back into the metal and oxygen. In such cases oxidation corrosion is not possible. For noble metals like Au, Ag and Pt oxidation corrosion is not possible because oxide layer formed is very unstable decomposes back into metal and oxygen.
- 3) If the metal oxide formed is volatile, it volatilizes as soon it is formed leaving underlying metal for further attack, therefore, rapid and continuous corrosion takes place. Molybdenum forms volatile oxide film of MoO_3 which accelerates further corrosion.
- 4) If porous oxide film is formed atmospheric oxygen can have access to the underlying metal surface through pores, hence continuous corrosion takes place. Porous oxide layer is formed by alkali and alkaline earth metals.

Pilling Bed worth Rule:

According to Pilling Bed-Worth Rule,

- ❖ If volume of metal oxide formed on the surface of a metal is more than or equal to the volume of metal from which it is formed, the oxide layer will be protective or non porous.
- ❖ If volume of metal oxide formed on the surface of a metal is less than the volume of metal from which it is formed, the oxide layer will be no- protective or porous.
- ❖ For example, specific volume ratio (volume of metal oxide /volume of metal) of W is 3.6, Cr = 2.0, Ni = 1.6. Hence, the rate of corrosion is very less in tungsten.

ii. **Corrosion by other gases:**

Gases such as Cl_2 , SO_2 , H_2S , NO_x , in dry atmosphere react with metal and form corrosion products, which may be protective or non-protective.

❖ Dry Cl_2 reacts with Ag and forms AgCl that is a protective layer, but when Cl_2 reacts Sn

forms $SnCl_4$ which is non – protective.

❖ In petroleum industries at high temperatures H_2S attacks steel forming FeS scale, which is porous.

iii. **Liquid metal corrosion:**

Liquid metal corrosion occurs when a liquid metal flows over a solid metal at high temperature.

Example: In nuclear reactors sodium metal corrodes the cadmium rods.

What is wet or electrochemical corrosion and explain principle involved in it?

Wet or Electrochemical corrosion:

Wet or electro chemical corrosion is common type of corrosion which occurs under wet or moist conditions. It is observed when (i) a metal is in contact with a conducting liquid , and/or (ii) dissimilar metals are dipped partially in aqueous corrosive environment.

The Wet or electrochemical corrosion involves:

1. Formation of anodic and cathodic areas
2. Presence of conducting medium
3. Corrosion of anodic parts only
4. Formation of Corrosion product closer to the cathodic area.

Explain electrochemical theory of corrosion by taking rusting of iron as an example.

Electrochemical theory of corrosion:

According to this theory, when a metal comes in contact with a conducting liquid a galvanic cell is formed within the metal. Some parts of the metal act as anode and rest act as cathode. Atmospheric gases and humidity present in the corrosive environment act as an electrolyte. Corrosion of anodic parts takes place due to oxidation at anode.

Electrochemical theory of corrosion is explained by taking rusting of iron as an example under different environmental conditions.

The anodic reaction involves oxidation of Fe to Fe^{+2}



The cathodic reaction depends on the availability of oxygen at different pH of the corrosive medium.

The cathodic reaction occurs in two ways (i) **hydrogen evolution** (ii) **oxygen absorption**

(i) Hydrogen evolution

This type mechanism occurs when,

- ❖ anodic areas are large and cathodic areas are small
- ❖ oxygen is absent

(a) In acidic medium:



(b) In neutral /slightly alkaline medium



In both acidic and neutral or slightly alkaline medium hydrogen (H_2) is evolved, therefore this type of corrosion is called as **hydrogen evolution type of corrosion.**

(ii) Oxygen absorption

This type mechanism occurs when,

- ❖ Anodic areas are small and cathodic areas are large
- ❖ Oxygen is present

(a) In acidic medium:



(b) In neutral /slightly alkaline medium



In both acidic and neutral or slightly alkaline medium oxygen is absorbed, therefore this type of corrosion is called as **oxygen absorption type of corrosion.**

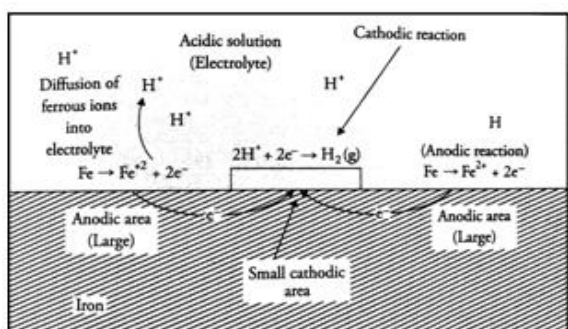


Fig (a) :Hydrogen evolution type mechanism

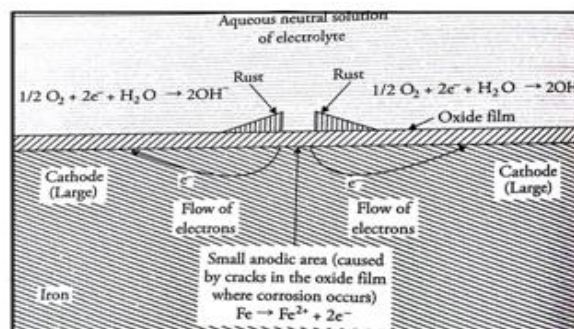
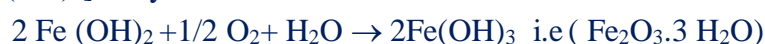


Fig (b):Oxygen absorption type mechanism

The Fe^{+2} ions, OH^- ions formed at anode and cathode respectively move in the opposite direction and meet at point which is closer to cathodic area to form ferrous hydroxide $[\text{Fe}(\text{OH})_2]$



In the presence of moisture and high oxygen supply, ferrous hydroxide is converted to hydrated ferric hydroxide $[\text{Fe}(\text{OH})_3]$ i.e. yellow rust .



If the oxygen supply is limited black anhydrous Fe_3O_4 is formed.

In general, the rate of corrosion of metals is much faster in acidic medium than in neutral or alkaline medium, but amphoteric metals like Al, Zn, etc, undergo corrosion with a faster rate even in basic

Types of electrochemical corrosion- Galvanic Corrosion, Differential aeration corrosion, Water line corrosion and pitting Corrosion.

Galvanic corrosion (Differential metal corrosion)

It is also called as *bi-metallic corrosion*. Galvanic corrosion occurs when two dissimilar metals (having different potentials) are electrically connected and jointly exposed to aqueous corrosive environment. The metal with the lower potential acts as anode and undergoes corrosion. The metal with higher potential acts as cathode and is protected.

Example: Iron pipes coupled with copper couplings.

In the above example, iron (-0.44V) acts as anode and undergoes corrosion because its potential is less than that of copper (0.34V). If anodic region is small it leads to severe corrosion.



Galvanic corrosion is controlled by (i) using a pure metal (ii) using metal closer in galvanic series (iii) Making sure that anodic metal should occupy large surface.

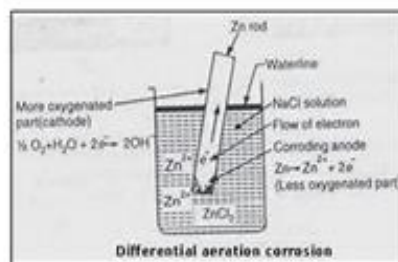
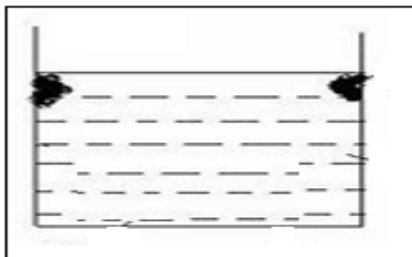
Differential aeration (oxygen corrosion cell) corrosion:

- ❑ It is a type of electrochemical corrosion that occurs when a metal in contact with conducting medium (corrosive medium) is exposed to *uneven supply of oxygen on its surface*.

- ❑ As a result of uneven supply of oxygen, an oxygen concentration cell is formed within the metal.
- ❑ **The part of the metal which is exposed to less oxygen concentration acts as ‘anodic area’ and gets corroded;** while the part of the metal which is exposed to relatively high oxygen concentration acts as cathodic area of corrosion cell is protected.
- ❑ *At anode (poorly oxygenated): $M \rightarrow M^{n+} + ne^{-}$*
- ❑ *At cathode (more oxygenated): $2 H_2O + O_2 + 4e^{-} \rightarrow 4OH^{-}$*
- ❑ *Examples of this type of corrosion include drop corrosion, crevice corrosion, waterline corrosion, pitting corrosion.*
- ❑ *Also the areas below nuts, bolts, joints, areas covered by dust particles and welded areas are suffered from this type of corrosion.*

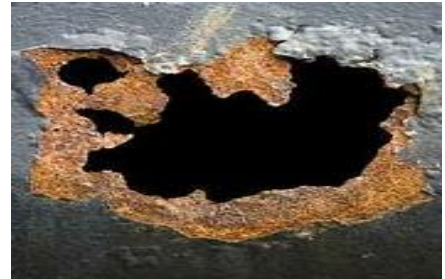
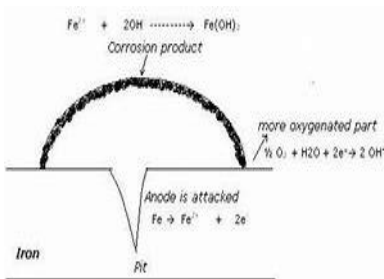
Waterline corrosion:

- ❑ Waterline corrosion a type of differential aeration corrosion.
 - ❑ It occurs when a metal is partly submerged in water or a metallic tank is partially filled with water.
 - ❑ *The Part of metal below waterline is poorly oxygenated and acts as anodic area; while the part of the metal above the waterline is more oxygenated and acts cathodic area.*
 - ❑ Corrosion occurs in the anodic area and simultaneously reduction of oxygen to OH^{-} ions occurs at cathodic area. The corrosion product is formed closer to cathodic area.
- This type of corrosion occurs in water tanks, ocean liners, etc.,.



Pitting Corrosion:

- ❑ Pitting corrosion is a localized form of corrosion resulting in the formation of pin holes or pits.
- ❑ When a small cracking, breaking of protective film on the metal surface occurs, small anodic areas and large cathodic areas are formed.
- ❑ The inner area of it is less aerated and the outer surface of the metal is well aerated.
- ❑ Therefore, the inner area of the pit acts as anode and under corrosion, while outer surface acts cathode and protected.
- ❑ Pitting may also be due to the galvanic corrosion;
 - (i) The preferential attack of the environment on a metal of an alloy may lead to pitting. E.g.; Alloy of Cu and Sn
 - (ii) The scratches on cathodic coatings also favor pitting.

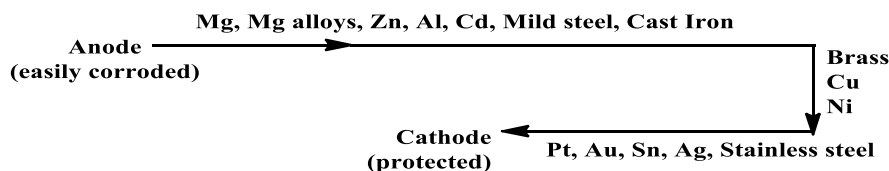


Factors affecting rate of Corrosion:

(a) Nature of metal

(i) Position of the metal in Galvanic Series:

Galvanic series gives real and useful information regarding the corrosion behaviour of metals and alloys in a given environment.



When two metals are electrically combined and exposed to corrosive environment the metal with lower potential acts as anode and undergoes corrosion where as the metal with higher potential acts as cathode.

- (ii) **Purity of metal:** In general higher the purity of the metal, lesser the rate of corrosion. Thus zinc of 99.95 % purity undergoes corrosion at rate of about 5000 times more compared to zinc of 99.999% purity.

(iii) Hydrogen Overvoltage:

If the hydrogen over voltage of the metal is low, the rate of corrosion will be high.

- (iv) **Relative areas of anode and cathode:** The rate of corrosion is more with the combination of a large cathodic area and small anodic area.

Therefore, Rate of Corrosion $\propto \frac{\text{Cathodic area}}{\text{Anodic area}}$

(v) Nature of surface oxide film

- If the corrosion product formed is stable, non-porous and strongly adherent layer it prevents further corrosion.
- If corrosion product formed is highly unstable the metals do not undergo corrosion.
- If the corrosion product formed is porous or volatile metals undergo severe corrosion.
- If the corrosion product is soluble in medium to which it is immersed, corrosion of the metal occurs with a faster rate.

(b) Nature of the environment

(i) Effect of humidity

Higher the humidity (moisture content) higher will be the rate of corrosion. Moisture acts as solvent for O_2 , H_2S , SO_2 etc to furnish the electrolyte essential for setting corrosion cell. Gases like H_2S and SO_2 increase the acidity of the medium by their dissolution in water. Therefore, the rate of corrosion increases as humidity increases

(ii) Effect of temperature: The rate of corrosion increases with an increase in temperature.

(iii) Effect of pH: The rate of corrosion of metals is much faster in acidic pH than in alkaline or neutral pH, but amphoteric metals like Al, Zn undergoes severe corrosion even in basic medium.

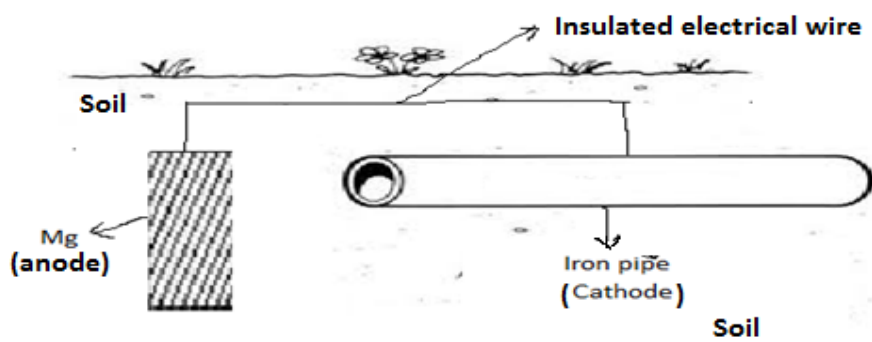
Corrosion control methods:

Cathodic protection:

The principle involved in this method is to force the metal to be protected (Parent metal) to behave like cathode. Therefore, corrosion of the parent metal is prevented. There are two types of cathodic protections, (a) Sacrificial anodic protection (b) Impressed current cathodic protection.

a) Sacrificial anodic protection

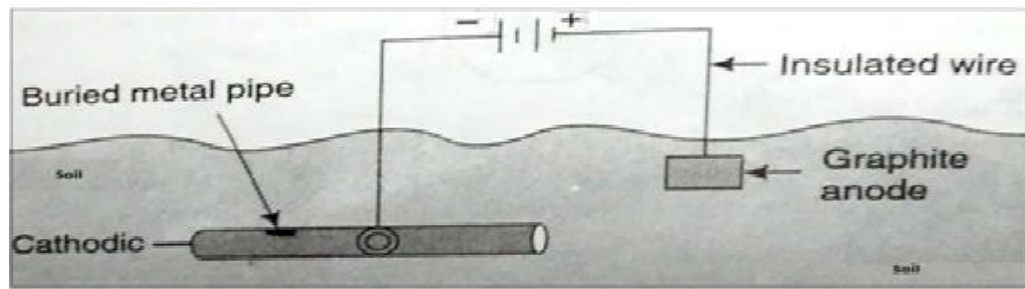
In this method, the metallic structure to be protected is electrically connected to a more active or anodic metal than the metallic structure to be protected. The more active metal acts as anode and gets corroded slowly; while the parent structure (metallic structure to be protected) is forced to act as cathode of galvanic cell, hence protected. As this more active metal is sacrificed its life in the process of saving metallic structure from corrosion, it is known as sacrificial anode and, therefore, this method is called as sacrificial anodic protection.



The metals which are commonly used as sacrificial anodes are Mg, Zn, Al and their alloys. This method is used to protect buried pipelines, underground cables, marine structures, ship hulls and metallic water tanks.

b) Impressed current cathodic protection

In this method, an impressed D.C current is applied, through D.C current source by a battery, between the metallic structure to be protected which is forced to act as cathode and an insoluble electrode like platinum, graphite or nickel which is buried in conducting medium adjacent to the metallic structure to be protected and acts as anode of an electrolytic cell as shown in the figure. The impressed D.C current applied nullifies the corrosion current thus the metallic structure is protected from corrosion.



The metals which are commonly used as insoluble anodes are Graphite, Scrap iron, etc. This type of cathodic protection is applied to buried structures such as tanks and pipelines, since, their operating and maintenance costs are less, and they are well suited for large structures and long term operations.

Surface Coating-Types

Metallic coatings

Anodic coatings Anodic coatings are produced from coating metals which are anodic to the base metal (i.e., Metal which is to be protected).

Coatings of Zn, Al and Cd on iron (or steel) are anodic because their electrode potentials are lower than that of the base metal iron.

If any pores, breaks occurs in such anodic coatings, a galvanic cell is formed the coating metal becomes anode and the base metal becomes cathode, hence protected.

Ex: Zn coating on iron

If any pores or breaks occur, Zinc acts as anode. Iron acts as cathode. Thus, no attack on the iron occurs, until practically the Zinc has corroded in the vicinity of the exposed part of iron.

Cathodic coatings;

Cathodic coatings are obtained by coating a more noble metal than the base metal. The coating metal protects the base metal because it has higher corrosion resistance than the base metal. If any pores, breaks occur in such cathodic coatings a galvanic cell is formed, the coating metal becomes cathode.

Ex: Tin coating on iron

If any pores or breaks occur, Tin becomes cathode and Iron becomes anode. Hence more and rapid corrosion takes place. Therefore, cathodic coating should be free from pores and breaks.

Methods of application of metallic coatings:

1. Electroplating:

Electroplating is the process of deposition of a coating metal on the base metal by passing direct current through an electrolytic solution which contains the soluble salt of the coating metal.

The process involves following steps

- A) Surface Preparation
- B) Electrodeposition

Surface Preparation: Before electrodeposition on the metal its surface is cleaned to remove any scale, dust, rust and oxides etc. The various methods employed for cleaning metal surface are—Mechanical cleaning, degreasing by organic solvents, Alkali cleaning, acid Pickling and etching, sand blasting.

Surface cleaning provides a smooth surface for electrodeposition and the deposit obtained is tough, adherent, smooth and bright in appearance.

Electrodeposition: it is the process of depositing the desired metal on the surface of the other metal.

Principle and procedure of electrodeposition: After surface cleaning, the article is made cathode in the electrolytic cell. The anode is the metal to be deposited or an inert material like graphite or lead-antimony alloy. The anode and cathode are dipped in suitable electrolytic solution and direct current is passed through it. Under the influence of electric current, the metal ion migrates to the cathode and get deposited on it.

Metal salt \leftrightarrow M^{n+} + nonmetal ion

$M^{n+} + e^- \rightarrow \text{Metal}$

These metal ions are continuously replenished by the dissociation of anode. If the anode is made of inert material like graphite, then electrolytic salt is added continuously to the electroplating bath to maintain the concentration.

Various factors improve the quality of the deposit such as: 1. Optimum current density

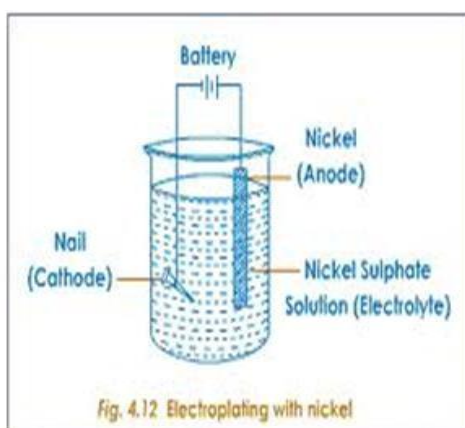
2. Adding various additives to the electrolytic bath to improve the quality of the deposit such as

boric acid, urea, glycine, gelatin for smooth, adherent and strong deposit 3. Adding aromatic sulphonates and thiourea for brightness 4. Adding levelers like sodium allyl sulphates for uniform deposit.

Ex: Electroplating of nickel

The article (metal) to be electroplated is first treated with organic solvent to remove oils, greases etc and then treated with dil. HCl to remove surface scales, oxides etc.

The cleaned article (metal) is then made as cathode of an electrolytic cell. The anode is pure nickel (at least 99% pure). The electrolyte is soluble salt of nickel (NiSO_4). The article to be electroplated (which is made as cathode) and pure nickel (anode) are dipped into electrolytic solution of NiSO_4 and connected to battery. When direct current is passed, Ni^{+2} ions migrate to the cathode and get deposited. Thus, a thin layer of nickel is deposited on the article (metal) which is made as cathode.



At anode: $\text{Ni} \longrightarrow \text{Ni}^{+2} + 2\text{e}^-$ (Oxidation)

At cathode: $\text{Ni}^{+2} + 2\text{e}^- \longrightarrow \text{Ni}$ (Reduction)

Nickel plating gives hard, adherent, high corrosion and wear resistant su

2. Electroless plating:

The process of deposition of a metal from its salt solution on a catalytically active surface with the help of a chemical reducing agent without using electrical energy is known as electroless plating.

Metal salt + Reducing agent \longrightarrow Metal plated over catalytic surface + Oxidised product

Electroless plating involves following steps

1. Preparation of active surface of base metal:

- By etching: Impurities on the surface of base metal can be removed by treatment with acids.
- Non conducting surfaces such as plastics and printed circuit boards are activated by treating them with SnCl_2 and PdCl_2 which results in the formation of a thin layer of Pd on the surface.

2. Electroless plating bath: Electroless plating bath consists of following components

- Soluble salt of the metal to be plated
- Reducing agent like formaldehyde or sodium hypophosphite
- Complexing agents like EDTA, Tartarates, Citrates etc.
- Exaltants like Succinates glycinates and fluorides to enhance the rate of plating.
- Stabilizers like thiourea, cations of calcium, thallium to prevent decomposition of plating bath solution.
- Buffer like Sodium acetate, boric acid to maintain the pH of bath solution.

Ex: Electroless Copper plating

Pre-treatment of surface:

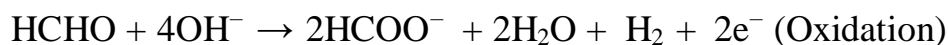
- Fe, Co and Ni can be directly plated without pre activation of surface.
- Non conducting surfaces such as plastics and printed circuit boards are activated by treating them with SnCl_2 and PdCl_2 which results a thin layer of Pd is formed on the surface.

Plating bath solution:

The surface activated metal (or article) is placed in bath of the following composition.

- i. CuSO_4 (12 g /L) – Provide metal ions.
- ii. Formaldehyde (8 g /L) - Acts as reducing agent.
- iii. EDTA (20 g /L) – used as complexing agent to get a homogenous smooth coating.
- iv. NaOH (15 g/ L) and Sodium potassium Tartarate (14 g /L) – used as buffer to maintain pH =11.
- v. Temperature of the bath is maintained at 25°C

The following reactions lead to the deposition of Cu on catalytically active surface;

**Applications:**

- i. Electroless plating is widely used in electronic applications. Electroless plating of nickel on Aluminium provides a non –magnetic underlay in magnetic components.
- ii. Plastic cabinets coated with Cu by electroless plating are used in digital and electronic instruments.

