

Most of the metals in nature exist in the combined forms as their oxides, carbonates, sulphides, chlorides or silicates. During extraction, these are reduced to their metallic states from their ores. For this extraction, considerable amount of energy is required. Pure metals can be regarded in excited state than their corresponding ores and they have a natural tendency to revert back to the combined state (lower energy state). Hence, when metals are put into use, they are exposed to the environment and begin to decay, more or less rapidly. This is called corrosion.

"Any process of destruction or disintegration and consequent loss of solid metallic material through an unwanted chemical or electrochemical attack by its environment, starting at its surface is called corrosion". Thus, corrosion is a process "reverse of extraction of metals".

Ex:- 1) Rusting of Fe, when exposed to atmosphere.
2) Formation of green film of basic carbonate ($\text{CuCO}_3 + \text{Cu}(\text{OH})_2$) on the surface of Cu, when exposed to moist air containing CO_2 .

Effect of Corrosion:-

- 1) Redn. of metal thickness leading to loss of mech. strength & structure failure.

- 2) Reduced value of goods due to deterioration of appearance.
- 3) The useful prop. of a metal such as malleability, ductility and electrical conductivity are lost.
- 4) Contamination of fluids in vessels and pipes.

Hence a knowledge of corrosion and its control will help to reduce the loss due to corrosion. It is better to control corrosion rather than preventing it because it is impossible to prevent corrosion.

Classification:

Based on the mechanism followed, corrosion may be classified into two types.

- 1) Dry or chemical corrosion or Direct chemical attack.
- 2) Wet or Electrochemical corrosion.

Dry or Chemical corrosion:

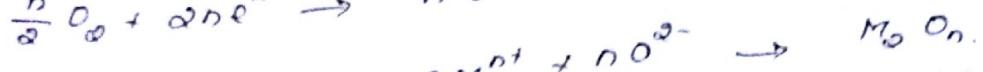
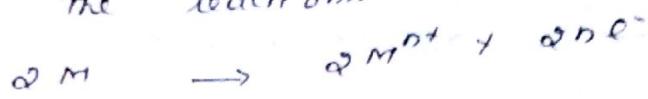
This type of corrosion is mainly caused due to the direct reaction of metal surfaces with the atmospheric gases like O_2 , CO_2 , H_2S , SO_2 , N_2 , Cl_2 etc. There are 3 main types of chemical corrosion.

- 1) Oxidation corrosion.
- 2) Corrosion by other gases.
- 3) Liquid - metal corrosion.

Oxidation Corrosion:

This is brought about by the action of clean metal surface with O_2 at low or high temp.. in the absence of moisture. Alkali & alkaline earth metals are quickly oxidised even at low temp.. All the other metals are oxidised at high temp..

The reactions are



(Metal oxide)

Mechanism:

Oxidation occurs first at the surface of the metal and the resulting metal oxide scale forms a barrier, which tends to restrict further corrosion. For oxidn. to continue, either the metal must diffuse outwards or the oxygen must diffuse inwards through the scale to the underlying metal. Both transfers occur, but the outward diffusion is more rapid than the inward diffusion due to smaller size and higher mobility of the metal ion.

Nature of the oxide film formed plays an important role. If the film is,

stable:

It means formation of an impermeable coating on the metal surface, which restrict further penetration of oxygen inside the metal. This film acts as a protective coating thereby shielding the metal surface.

Ex : Al, Sn, Pb, Cu, Pt etc are stable oxides.

2) Unstable :-

i.e. the oxide layer formed decomposes back into the metal and oxygen.



∴ oxidation corrosion is not possible in this case.

Ex : Au, Ag, Pt do not undergo oxidation corrosion.

3) Volatile :-

The oxide layer evaporates as soon as it is formed, leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, leading to excessive corrosion.

Ex : MoO_3 is volatile.

4) Porous :-

The oxide layer formed has pores or cracks through which atmospheric oxygen can penetrate through the surface of the metal and continue until the whole metal is converted into metal oxide.

Pilling - Bedworth Rule :-

According to Pilling - Bedworth rule, "an oxide is protective or non-porous, if the volume of the oxide is greater than the volume of the metal from which it is formed".

On the other hand, "if the volume of the oxide is less than the volume of the metal, the oxide layer is porous and hence non-protective".

i) Protective is non-porous: Al_2O_3 whose volume is greater than the volume of the metal Al. i.e. an extremely strong non-porous layer is formed thereby decreasing the rate of oxidation.

ii) Non-Protective is porous: Alkali is alkaline earth metals (like Li, K, Na, Mg) form oxides of volume less than the volume of the metals. This layer is affected by stress and strains thereby developing cracks & pores in its structure. Thus corrosion continues non-stop.

Corrosion by other gases:

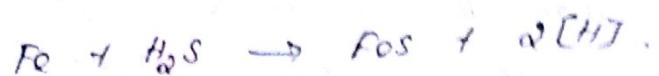
Gases like CO_2 , Cl_2 , F_2 , H_2S , SO_2 etc will also attack the surface of the metals leading to corrosion. In these cases the effect of corrosion mainly depends on the chemical affinity between the metal and the gas involved.

ii) If the film formed is protective and non-porous, the extent of attack decreases, because the film formed protects the metal from further attack.
Ex!: AgCl film.

a) If the film formed is non-protective or porous, the extent of attack increases and the surface of the whole metal is destroyed.
Ex!: Dry Cl_2 gas attacks Sn forming volatile SnCl_4 .

Corrosion by Hydrogen gas :-

It is a kind of corrosion due to hydrogen gas. When metal is exposed to hydrogen environment like H_2S , this causes the evolution of H_2 at the metallic surface.



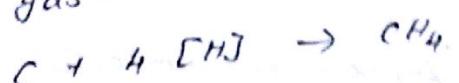
This atomic hydrogen diffuses inside the metal easily and gets collected in the voids present inside the metal where it recombines to produce H_2 molecule. This H_2 gas leads to cracking or blistering of the metal at high pressure which reduces the strength and activity of the metal.

Decarburisation :-

Presence of C in steel gives sufficient strength to it. When steel is exposed to H_2 environment at high Temp., atomic hydrogen is formed.



This reacts with C in steel and produces methane gas.



Hence, the carbon content of steel is decreased. Collection of this gas inside the steel leads to cracking. In this way steel loses its strength and is termed as decarburisation.

3. Liquid Metal Corrosion:

It is due to the chemical action of flowing liquid metal at high temp. on solid metal or alloy. This type of corrosion occurs in nuclear power reactors. This corrosion involves either i) dissolution of solid metal by a liquid metal or ii) internal penetration of the liquid metal into the solid metal.

Both these modes will lead to the working of the metal.

Wet Corr. / Electrochemical Corrosion:

This type of corrosion occurs,

- When a metal is exposed to an electrolyte with varying amount of oxygen.
- When two dissimilar metals or alloys are in contact with each other in presence of an aqueous solution or moisture.

Mechanism:

Corrosion occurs due to the existence of separate anodic & cathodic areas between which current flows through the conducting solution.

At anodic area,

Oxidation takes place by the liberation of free e^- s and the metal ion is destroyed either by dissolving or to the combined state.



M^{n+} $\xrightarrow{\quad}$ Dissolves in soln.

$\xrightarrow{\quad}$ Forms compd. like oxide.

Hence, corrosion always occurs at anodic areas.

At cathodic area,

Redn. rxn. taken place by H₂ gain
of e⁻s either by:

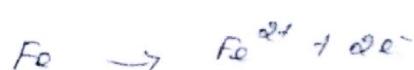
a) Evolution of Hydrogen or

b) Absorption of oxygen, depending upon the
nature of the corrosive environment.

Hence the metallic ions (at anodic part) and non-metallic ions (OH^- or O^{2-}) (at cathodic part) will diffuse towards each other through the medium and form a corrosion product somewhere between anode and cathode.

a) Evolution of Hydrogen:

It occurs usually in acidic environments. Considering Fe, the anodic reaction is dissolution of Fe as Fe^{2+} ions with the liberation of e⁻s.



These e⁻s flow through the metal, from anode to cathode, where H⁺ ions are eliminated as hydrogen gas.



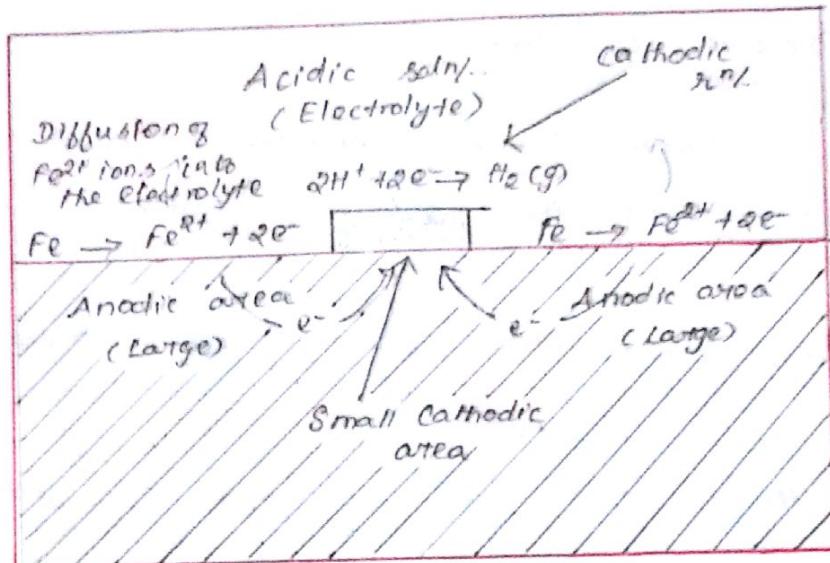
The over all reaction is,



This type of corrosion caused "displacement of H⁺ ions from acidic soln. by metal ions". Consequently all metals above hydrogen in the emf series have a tendency to get dissolved in acidic soln.

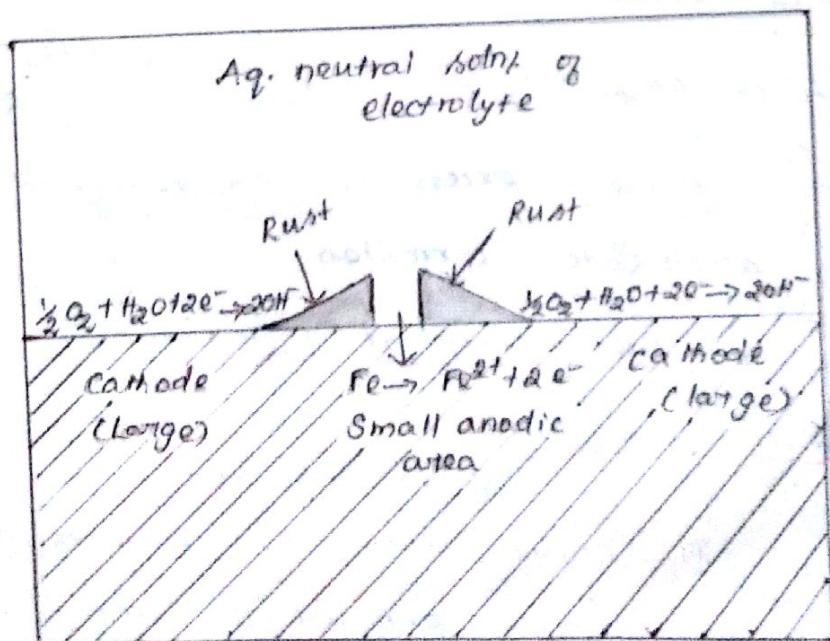
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with simultaneous evolution of hydrogen. In hydrogen evolution type corrosion usually the anodes are very large areas and the cathodes are small areas.



b) Absorption of Oxygen:-

This type will take place on the metal surfaces in neutral parts or weakly alkaline environment with oxygen.

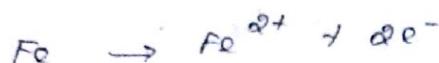


The formation of anodic area, on the metal surface is due to various factors like,

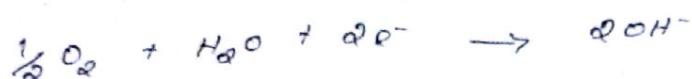
1. Partial roughness of metal surface.
2. Minute cracks on the surface.
3. Presence of impurities.

When Fe is exposed to neutral or alkaline environment the following reaction takes place.

At anode liberation of e^- s takes place.



At cathode e^- s are absorbed as follows.



Fe^{2+} & OH^- ions are attracted to the metal surface to form the product ferrous hydroxide.



Finally with more oxygen and moisture ferrous oxide is easily oxidised to $Fe(OH)_3$.



Rust.

Hence excess of oxygen and moisture greatly accelerate corrosion.

Types of Electrochemical Corrosion:

Galvanic Corrosion:

It is also known as Bimetallic corrosion. It occurs when two dissimilar metals are connected and exposed to corrosive environment. The less noble metal undergoes corrosion.

and more noble metal is cathodically protected by the galvanic current.

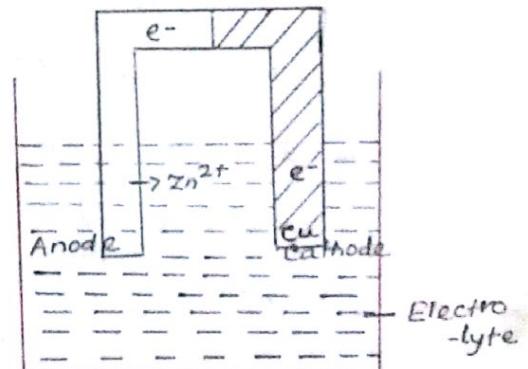
In case of Zn & Cu , Zn will act as anode (higher in electrochemical series) and undergoes corrosion whereas Cu (lower in electrochemical series) acts as cathode and is not affected.

Current flows from anode to cathode, corrosion takes place at anode while cathodic metal is not affected.

Prevention :-

It can be prevented by

1. Selecting two metals, which are very close in their electrode potential.
2. Providing an insulating material to the two metals.

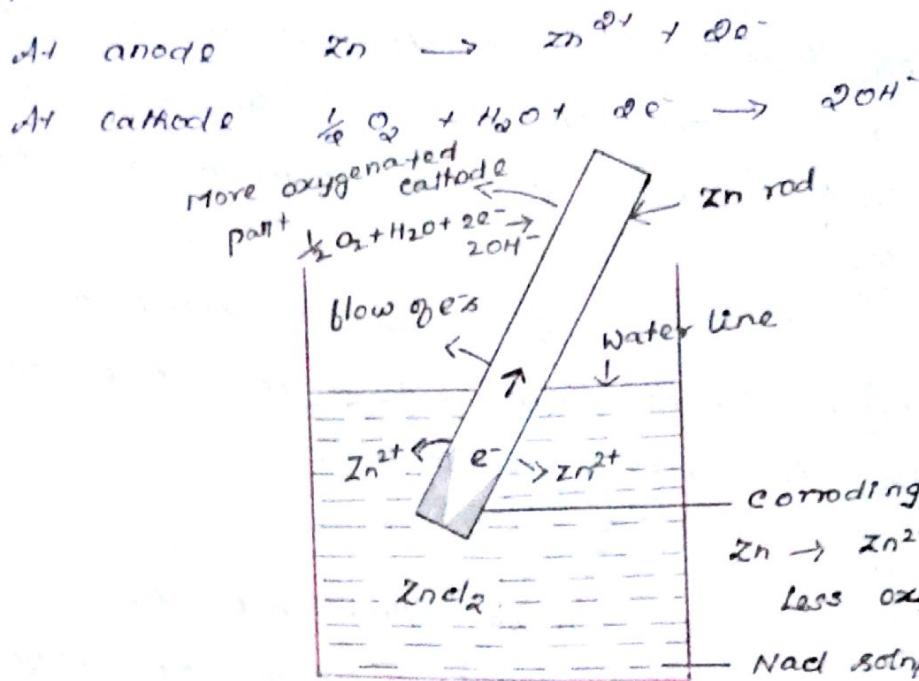


Differential Aeration Corrosion :-

This occurs when different parts of the metal are exposed to different air concentrations.

If a metal is partially immersed in a dilute soln. of $NaCl$, the parts above and closely adjacent to the water-line are more exposed to oxygen and hence become cathodic. On the other hand parts immersed to

greater depth have exposed to less oxygen conc. become anodic. Zinc dissolves at the anodic areas.

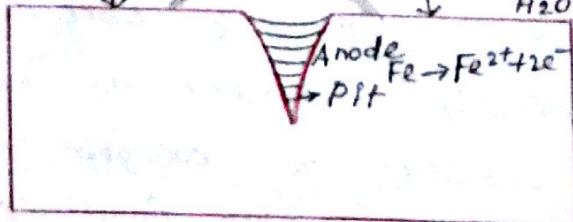
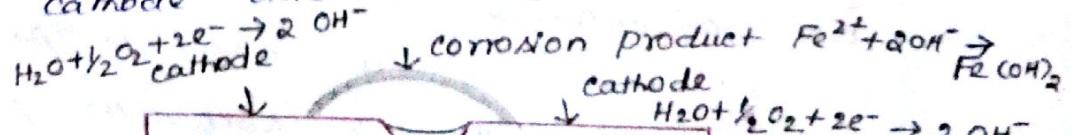


Example 3 Differential Aeration Corrosion:

Pitting Corrosion:

It is a localised accelerated attack resulting in the formation of cavities around which the metal is relatively unattacked. This results in the formation of holes or cavities in the metal.

Let us consider a water drop resting on the metal surface. The area covered by water drop acts as anode due to less oxygen conc. and suffers corrosion. The uncovered area acts as cathode due to high oxygen conc..



Water line corrosion

When water is stored in a steel tank, it is seen that the minimum amount of corrosion takes place along a line just below the level of water meniscus. The area above the water line (highly oxygenated) acts as cathode and is completely unaffected.

poor oxygenated
anodic part
corroded.
 $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
 $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2$

Highly oxygenated
cathode
 $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$

Stress corrosion

This type of corrosion is seen in fabricated articles of certain alloys (like In brasses and Ni brasses) due to the presence of stress caused by heavy working. Hence pure metals are relatively immune to corrosion. Stress results in the formation of cracks which grows and propagates till failure occurs.

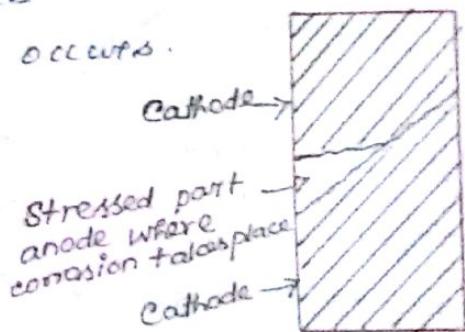
Ex: Caustic embrittlement,

occurring in mild steel

when exposed to alkaline

solns., at high temp. and stressed.

Boiler water usually contains certain proportion of Na_2CO_3 , added for water softening purposes. In high press., boilers, this breaks up to give NaOH & CO_2 , and makes boiler water alkaline.



Factors Influencing Corrosion:

Corrosion takes place in the metal

due to the influence of its environment. Corrosion mainly depends on

- 1) Nature of the metal
- 2) Nature of the environment.

Nature of the metal :- 1. Position in Galvanic series:-

Metals with negative electrode potential (compared to hydrogen) in electrochemical series is in galvanic series are more prone to corrosion. These metals are highly reactive in nature and they behave as anodes. On the other hand metals with positive electropotential are less prone to corrosion. They behave as cathodes and are less reactive.

2. Over voltage:-

When Zn metal is placed in 1N H_2SO_4 soln., it undergoes corrosion forming a film evolving hydrogen gas. The initial rate is slow because of high overvoltage of Zn metal ($= -0.70\text{ V}$). If few drops of $CuSO_4$ are added, the corrosion rate is accelerated because some Cu gets deposited on Zn metal forming minute cathodes, where the H_2 overvoltage is -0.33 V . Thus, redn. in overvoltage of the corroding metal accelerates the corrosion rate. Cu will get at thereby reducing the anti-oxidative voltage will be

3. Relative areas of anode and cathode:

When two dissimilar metals are in contact, corrosion in the anodic area will be directly proportional to the ratio of areas of cathodic part and the anodic part.

Corrosion will be severe if the anodic area is smaller and cathodic area is larger. The larger cathodic area will create a great demand for e^- which can be satisfied by smaller anodic area by undergoing further corrosion.

4. Purity of Metals:

Impurities in a metal generally causes, 'heterogeneity' and thus tiny electrochemical cells are formed and the anodic part gets corroded.

Ex.: Zn metal containing impurities such as Pb or Fe undergoes corrosion due to the formation of local electrochemical cells.

5. Physical state of metals:

The rate of corrosion is influenced by physical state of the metal like grain size, orientation of crystals, stress etc. The smaller the grain size of the metal, the greater will be its solubility and hence greater will be its corrosion. Also, areas under stress, even in a pure metal tend to be anodic and corrosion takes place at those areas.

6. Nature of the surface film:-

In aerated atmosphere, normally all metals get covered with a thin surface film of metal oxide. Metals like Mg, Fe etc form oxides whose specific volume is less than the volume of the metal. Hence, the oxide film formed will be porous and more oxygen diffuses inwards leading to more corrosion.

Metals like Cr, Al, Ni etc form oxides whose specific volume is greater than that of the metal atom. This oxide film is compact and impervious and corrosion will be prevented.

7. Nature of corrosion product:-

In electrochemical corrosion, if corrosion product is soluble in the corroding medium, corrosion proceeds at a faster rate. On the other hand if the product is insoluble or it interacts with the medium to form another insoluble product which will act as a barrier thereby suppressing further corrosion.

Nature of the Environment:-

1. Temperature:-

Increase in temp. increases the reaction rate as well as the diffusion rate and hence the rate of corrosion is increased.

2. Humidity :-

Humidity is directly proportional to the corrosion rate. It is the deciding factor of atmospheric corrosion. The basic requirement for enhancement of corrosion in humid conditions is that atmospheric gases like CO_2 , O_2 etc, dissolve in water to produce the electrolyte which is essential for electrochemical corrosion.

3. Presence of corrosive gases :-

In the industrial area, the atmosphere is polluted with CO_2 , SO_2 , H_2S & fumes of HCl , H_2SO_4 etc. These gases produce electrolytes which are acidic thereby increasing atmospheric corrosion. Similarly marine atmosphere contains more Cl^- ions which also increase the corrosion rate.

4. Presence of solid suspended particles :-

If the suspended particles are chemically active like NaCl , $(\text{NH}_4)_2\text{SO}_4$ etc, they absorb moisture and act as strong electrolytes, thereby increasing corrosion rate.

If the suspended particles are chemically inactive like charcoal, they absorb both S gases and moisture which also slowly increases the corrosion rate.

5) Effect of pH :

Generally acidic medium is more corrosive than alkaline medium.

The corrosion rate of Fe in oxygen free water is slow at $pH < 5$. But the corrosion rate is much higher in presence of oxygen. Consequently corrosion of metals can be reduced by increasing the pH of the attacking environment.

Ex! Zn is readily corroded in acidic soln. suffers very less corrosion in alkaline medium ($pH = 11$)

6) Nature of the ions present:

Anions like silicates when present in the medium lead to the formation of insoluble reaction products, which stop further corrosion. Whereas the Cl^- ions in the medium destroy the oxide film and expose the metal for further corrosion.

Corrosion Control:

Prevention of corrosion is very important as it is very harmful for metals causing huge losses to industries. This can be controlled in several ways.

1. Proper designing: The design of the material should be such that, if corrosion even if it occurs, is uniform and does not result in intense and localised corrosion.

Some of the design principles are,

a) Avoid contact of two dissimilar metals in presence of a corroding medium.

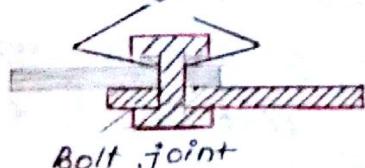
b) When two dissimilar metals are in contact, the anodic material should be large in area whereas cathodic metal should be smaller.

c) If two dissimilar metals are in contact, they should be as close as possible to each other in electrochemical series.

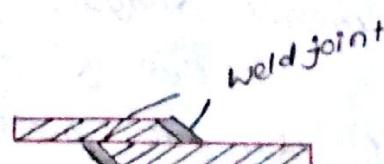
d) Whenever the direct joining of dissimilar metals is unavoidable, an insulating fitting may be applied in order to avoid direct contact between them.

e) Bolts & rivets are undesirable since crevices permit concentration differences.

crevices

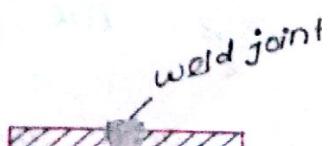


Bolt joint



Good design

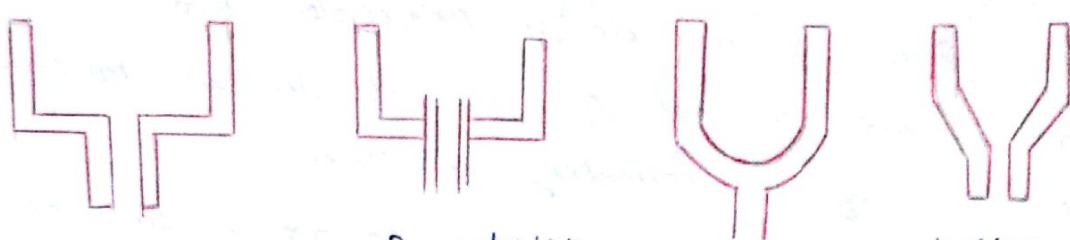
weld joint



Best design

g) During designing the tank and containers, care should be taken in fixing the outlet pipe at the bottom so that the liquid can be drained completely.

g) Sharp corners and edges should be avoided because they favour the formation of stagnant areas and accumulation of solids etc.



2. Use of Pure metals:-

Impurities of a metal cause heterogeneity, which decreases the corrosion resistance of the metal. This may be improved by increasing its purity. Purification of metals like Al, Mg etc makes them corrosion resistant by protective oxide film formation. But production of pure metals is costly and also the metal loses some of its mechanical properties.

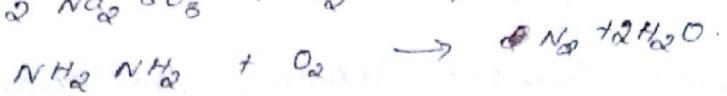
3. Use of metal alloys:-

Use of metal alloys is a very good method for the protection of metals against corrosion. By alloying metals like Pb, Cu etc with noble metals, the anodic activity of these metals will be lowered resulting in the control of corrosion. Cr is the best alloying metal for Fe B steel.

Change of corrosive environment :-

i) Removal of oxygen :-

Removal of oxygen from water system will prevent corrosion as corrosion rate is slow in free oxygen free water. It can be achieved by the use of strong reducing agents like $\text{Na}_2\text{S}_2\text{O}_3$ or hydrazine.



ii) Dehumidification :-

One of the reasons for corrosion to occur is moisture. So, it can be controlled by using substances which can act as dehumidifiers.

Ex: Alumina, Silica etc.

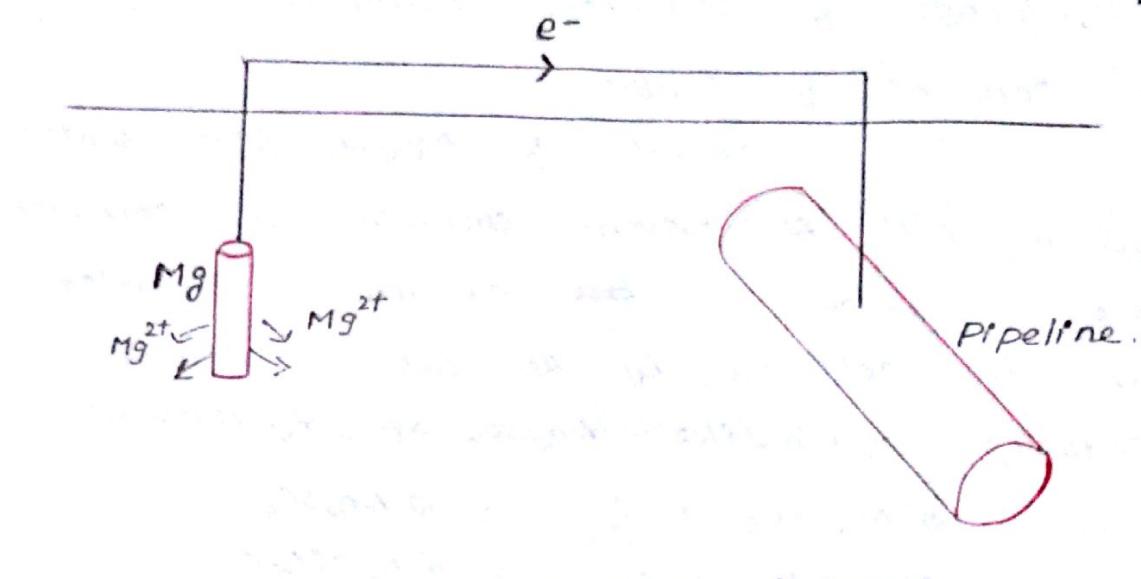
Electrochemical technique : (cathodic protection). This involves two methods.

iii) Sacrificial Anode Method :-

In this method, the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal will act as anode thus forcing the parent metal to act as cathode. The more active metal corrodes slowly and this metal is called sacrificial anode. This corroded sacrificial anode is replaced by a fresh one, when consumed completely.

Ex: Mg, Zn, Al and their alloys.

Applications: Protection of buried pipeline, underground cables, marine structures, ship-hulls, water tanks etc.

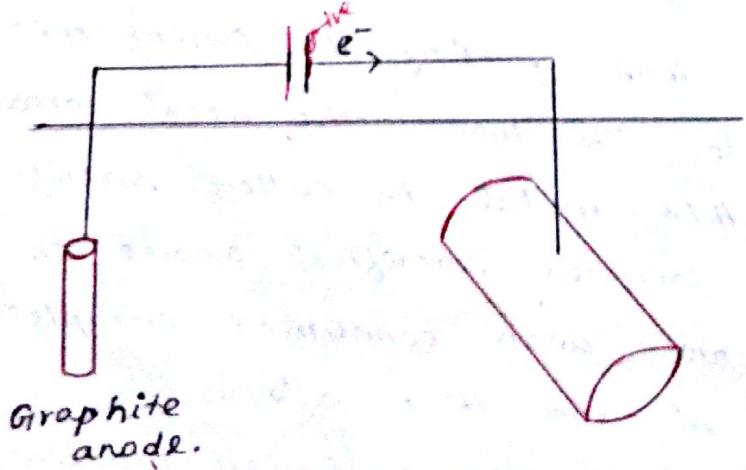


2) Impressed Current Cathodic Protection:

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and converting the corroding metal from anode to cathode. The impressed current is derived from a direct current source like battery or line with an insoluble anode like graphite or Pt. Usually a sufficient d.c current is applied to an insoluble anode buried in the soil and connected to a metallic structure to be protected. This anode is immersed in a backfill (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil.

Applications:

Water tanks, buried oil or water pipes, condensers, transmission line towers, etc.



Use of Corrosion Inhibitors

This is a method of protecting the environment. Selected chemicals known as corrosion inhibitors are added to the environment which stop the anodic or cathodic reactions. These are classified as follows:

1. Anodic & Cathodic & 2. Vapour phase inhibitors.

1) Anodic Inhibitors

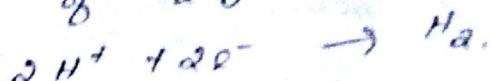
This type of inhibitors combine with the anodic metal forming an oxide film or layer which acts as a barrier. These inhibitors should be added in enough amounts to cover the metal surface completely with the oxide film. Otherwise corrosion will be concentrated on the remaining areas resulting in pitting.

Ex!: chromato, phosphate, molybdate, tungstate etc.

2) Cathodic Inhibitors

These are used, depending upon the environment. For cathode, there are two types of environment namely acidic and neutral environment.

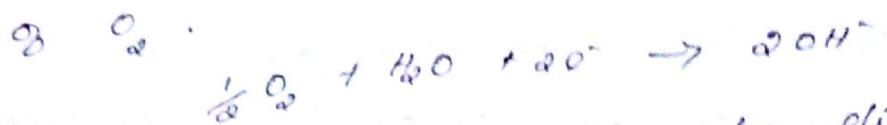
a) In acidic soln. the cathodic eqn. is the liberation of H₂ gas.



Corrosion can be controlled by slowing down the diffusion of H⁺ ions through the cathode.

Ex!: Amines, Mercaptants, Thio urea etc.

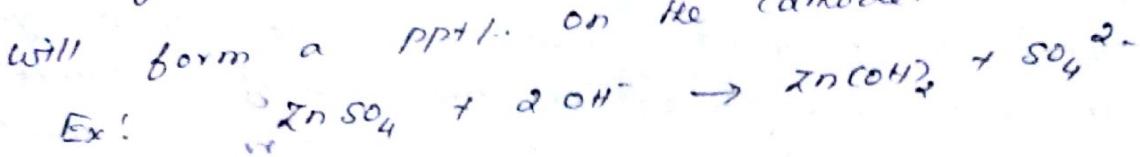
b) In neutral soln. cathodic % is absorption



Corrosion is controlled either by eliminating O_2 from the corroding medium or by decreasing the diffusion rate.

Dissolved O_2 can be eliminated by adding reducing agents like Na_2SO_3 , NH_4^+ etc.

Diffusion of O_2 can be controlled by adding inhibitors like Mg , Zn , Ni salts which will form a ppt. on the cathode.



3. Vapour Phase Inhibitors:

Most important among the common vapour phase inhibitors.

-idal inhibitors are the vapour phase inhibitors. These are organic inhibitors which are readily vapourised and form a protective layer on the metal surface. These are used to prevent corrosion in closed equipments, packing materials, sophisticated instruments etc.

Ex: Dicyclo hexyl ammonium nitrate, phenyl thio urea, β benzotriazole.

Surface treatment for metallic coating:

(14)

The surface of the metal is usually covered with rust, scales, oil, grease etc. Before plating, these impurities should be removed completely in order to achieve the effectiveness. For getting smooth, uniform and adherent coating, the above impurities are removed by anyone of the following methods.

- 1) Physical cleaning
- 2) Chemical cleaning
- 3) Mechanical cleaning.

1) Physical Cleaning:

In this process, the metallic surface is made free from oil, grease, dirt and dust.

a) Degreasing:

Oil and grease present on the metal surfaces are removed by using organic solvents such as trichloroethylene, toluene, acetone and CCl_4 .

b) Bleaching:

This process consists of immersing the article in dil. HCl , or H_2SO_4 or mixture of dil. HNO_3 & dil. H_2SO_4 to remove heavy scale of oxidized rust on the metallic surfaces.

Chemical cleaning :-

a) Alkaline Treatment :-

It is the most common cleaning technique used to remove surface scale. Alkaline cleaners include NaOH , Na_2WO_4 , Na_3PO_4 , Na_2SiO_3 etc.

b) Acid Pickling :-

Oxide scales, rust and corrosion products are removed by this method.

Iron and steel parts are dipped in a pickling bath containing 5% H_2SO_4 at 75°C to remove the mild scales.

Brass and Bronze metals are dipped in a mixture of HCl & H_2SO_4 & a small amount of HNO_3 to remove the scales.

c) Rinsing :-

During electroplating rinsing with clean water is essential between various steps.

Mechanical Cleaning :-

In this method the loose rust, oxide scales and corrosion products are removed from the metal surface by mechanical cleaning such as hand brushing, wire brushing, grinding, polishing etc.

a) Flame Cleaning :-

This process is done by passing high velocity hot flame over the metal surface. It is applied to remove moisture and loosely adhering scales.

b) Sand Blasting :-

Oxide scales present on the steel surfaces are removed by using this method. This process involves the addition of sand into air stream under the pressure of 100 atmospheres.

c) Etching :-

It is a final process of the metal surface which offers better adhesion and improved appearance of coating.

Electroplating :-

It is the process by which the coating metal is deposited on the base metal by passing direct current through an electrolytic soln., containing no soluble salt of the coating metal.

In this method, the freshly cleaned base metal (to be plated) is made as cathode and the metal being deposited made as anode. Anode may be either coating metal or inert material in the electrolytic cell. The nature of the deposit depends on,

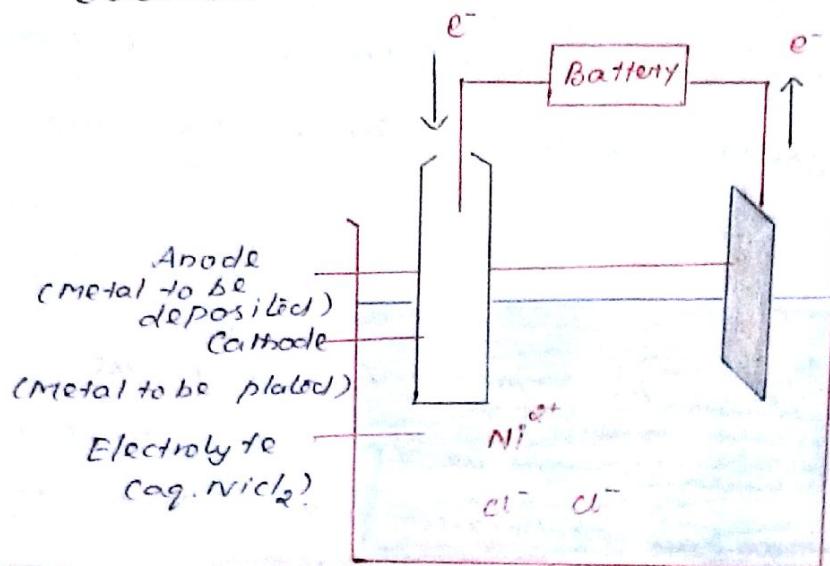
- 1) The current density.
- 2) The bath composition.
- 3) The temperature.
- 4) The presence of other additives.

Objectives :-

1. To increase the surface properties of metal and non-metal.

- a) To get improved appearance on the base metal.
- b) To increase resistance to corrosion, chemical attack and wear resistance.
- c) To increase decorative and commercial values of the metal.

Procedure:



The article to be plated is first subjected to pretreatment processes like degreasing, alkaline cleaning, acid pickling etc. The cleaned articles are then made as cathode and anode is either the coating metal itself or the inert material. These metals are placed in a suitable salt bath which serves as an electrolyte. The anode and cathode are connected to the positive and negative terminals. Plating is then carried out at a proper voltage and current density of 0.5 to 1.5 amp/cm² to get smooth and uniform deposit. The thickness of the deposit ranges from 0.01 to 100 μm , and the required time ranges from few second to 30 mins.

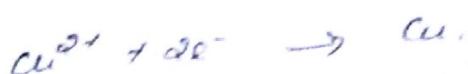
Expt. Copper plating

Copper plating of a material is done by choosing copper sulphate as the electrolyte, copper rod as anode and the material to be plated as cathode.

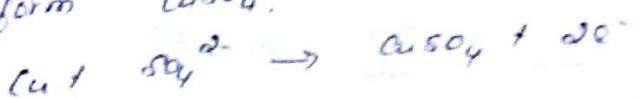
In electrolyte, the following ionisation will take place:



While passing current Cu^{2+} from the electrolyte gets deposited at cathode.



The free SO_4^{2-} ion migrates towards the anode and removes an equivalent amount of Cu to form CuSO_4 .



For Cu coating acid bath contains:

For Cu coating acid bath contains 2.5 to 5% conc. H_2SO_4 .

15 - 30% of CuSO_4 & additives like boric acid, with small amt. of gelatin etc are mixed and used as electrolyte.

For Ni:

Electrolyte - NiSO_4 pH - 4.5

Temp. - 40 - 50 °C. Appl. : Undercoat for Cr plating.

Current density - 0.6 amp/cm².

For Cr:

Electrolyte - $\text{Cr}_2(\text{SO}_4)_3$ (or) Cr_2O_3 .

Temp. - 40 °C.

current density - 0.6 amp/cm².

Applications: Corrosion resistant and decorative finish on Fe objects.

Factors Affecting Electroplating :-

1. Cleaning of the articles is very important before electroplating.
2. Thickness of the electrolyte film should be minimized in order to get a strong adherent coating.
3. pH of the electrolyte should be maintained properly.
4. Additives are added to get strong & smooth coating. These should be used in small amounts.

Electroless plating :-

It is a technique of depositing noble metals from their salt solns. on a catalytically active surface of less noble metal by using a suitable reducing agent without using electrical energy. Reducing agent reduces the metal ion into metal.

Various aspects of electroless plating are,

1. Preparation of active surface :-

a) Etching - Removal of impurities by acid treatment.

b) Electroplating - A thin layer of the metal to be plated or any other suitable metal is coated on the surface of the object.

c) Treating with stannous chloride followed by dipping in palladium chloride soln.

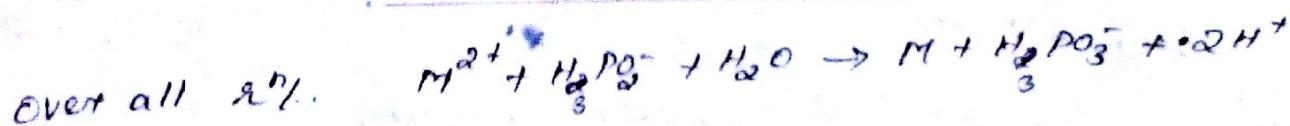
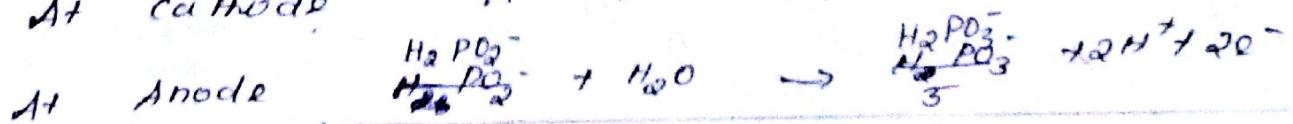
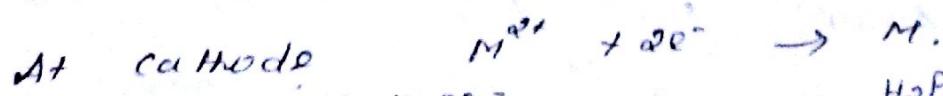
This method is used only for plastics and printed circuit boards.

a) Plating Bath :-

- Coating metal - Soluble salt of the metal to be plated.
- Reducing agent - Formaldehyde, Hypophosphite etc.
- Complexing agent - For improving the quality of the deposit.
Ex: Tartrate, Citrate, Succinate
- Exaltant - For enhancing the plating rate.
Ex: Fluoride, Glycinate etc.
- Stabilizer - For preventing the decomposition of plating bath soln.
Ex: Thiourea, Ca, Zn.
- Buffer soln. - For controlling the pH of the bath.
Ex: Soda acetate + Soda Hydrogeno + Rochelle salt.

Procedure :-

The object to be plated is dipped in the bath containing the salt of the metal and reducing agent. The metal ion in the soln. is reduced to the corresponding metal and is plated over the surface of the object.



Example: Electroless Ni plating

It involves the reduction of Nickel ions in an aqueous soln. followed by the deposition of Ni metal without the use of electrical energy. The reducing agent used for electroless plating is hypophosphite. Ex: The metals & alloys of Al, Cu & brass can be Nickel plated without any activation.

Plating bath:

Coating metal : Nick soln. 20 g/l.

Reducing agent : Sod. Hypophosphite 20 g/l.

Buffer : Sod. Acetate 10 g/l.

Complexing agent : Sod. succinate 15 g/l.

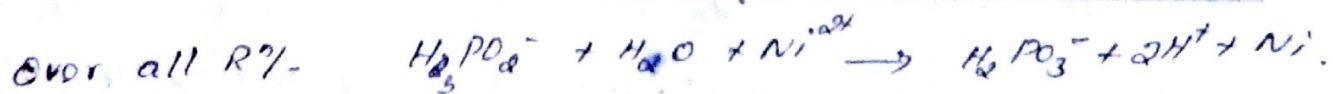
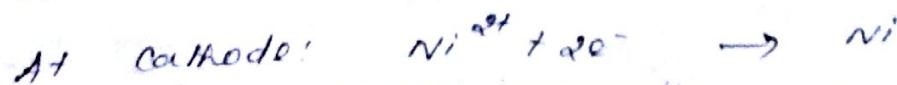
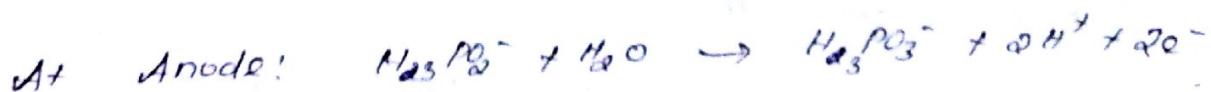
Exaltant : Succinate Fluoride 15 g/l.

Optimum pH : 4.5

Optimum Temp : 93°C

Procedure:

The object is immersed in the plating bath. During the process reduction will occur and Ni gets coated over the object.



Applications of Nickel plating:

1. Mainly used in electronic appliances.
2. Possesses better corrosion resistance.
3. Deposition in non-conductors like ~~plastic~~ is possible.

Advantages of Electroless plating over Electroplating.

1. No electrical energy is required.
2. Electroless plating on insulators (plastics, glass) and semi conductors are easily carried out.
3. Electroless plated materials possess unique features.
4. Complicated parts and complex shapes can be plated uniformly.
5. Electroless Ni coated polymers find decorative as well as functional applications.
6. Electroless plated materials possess better throwing power. i.e. ability of the electrolytic cell to give a deposit of uniform thickness over the entire cathode area.

Surface or chemical conversion coating!

When the metal coats are not adherent and not resistant to corrosion, they can be converted into insoluble compounds like oxides, phosphates etc. and this process is known as surface conversion coatings.

Such coatings are used as excellent bases for paints, lacquers & enamels

Some important chemical conversion coatings are

a) Galvanising.

1. Anodising.

b) Tinning.

2. Phosphate coatings.

3. Chromate coating

4. Hot dipping.

Anodising:-

It is an electrochemical process by which a thick oxide coating can be produced on the base metal like Al, Zn and Mg by making it as anode.

During electrolysis the oxide film is formed at the surface. It may be porous and this can be sealed by dipping the metal in boiling water. This treatment changes porous oxide into its mono hydrate which occupies more volume and thereby the pores are sealed.

Ex:- Anodising on Al.

Anode - Aluminium.

Cathode - Inert metal (Steel or Cu).

Electrolyte - Chromic acid & H_2SO_4 .

Temp. - $50 - 55^\circ C$.

Current density - $10 - 15 \text{ mA/cm}^2$.

Advantages:-

1. These are superior than natural oxide films.
2. These coatings possess better corrosion resistance.
3. The oxide film produced is protective and non-porous.

Uses:-

1. Used in domestic articles like water jugs, ornaments etc.
2. Anodised Al is used in automobile engine piston.

2. Phosphate Coatings:

Phosphate coatings are formed by the reaction of base metal with e.g. soln. of phosphoric acid and phosphates of Zn, Fe or Mn along with accelerators.

The chemical rxn. between the base metal and the phosphate soln. results in the formation of a surface film. This forms an adherent coating over the base metal. These ~~are~~ coatings are grey in colour.

Such coatings are applied commonly to steel, Fe & Zn and to a lesser extent to Al, Cd and Sn. These are applied by immersion, spraying or brushing method. These do not offer complete resistance to atmosphere and used as primer-coat.

3. Chromate Coating:

These are produced by immersion of the article in K_2CrO_4 bath followed by neutral chromate soln. As a result a surface film consisting of a mixture of trivalent & hexavalent Chromium is formed. These are used as base for paints, lacquers and enamels.

4. Hot dipping:

It is a process of producing a coating of low melting metal (Zn, Sn, Pb, Al etc) on the surface of Fe, steel & Cu which have relatively high melting points. In this process, base metal is immersed in a bath of

molten coating metal and form a coating uniformly.

Ex: a) Galvanising:

It is a process of coating Fe or steel surface with Zn to prevent them from rusting.

Procedure:

Fe or steel surface is first cleaned by pickling with dil. H_2SO_4 for 15-20 mins at 60-70°C which removes scales and rust. Then it is dipped in a bath of molten Zn maintained at 425-430°C. The surface of the bath is covered with flux ($CaHgCl_2$) to prevent oxide forming and form a thin layer of Zn.

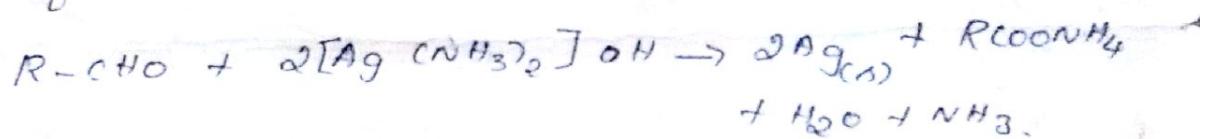
b) Tinning:

Process of coating tin over Fe.

Before coating, the surface of the ^{metal} filo is cleaned by using dil. H_2SO_4 to remove any oxide film. Then it is passed through a bath of zinc chloride flux and then to a tank consists of molten tin and finally through the rollers which remove excess of tin and produce thin and uniform coating of tin on steel surface.

- Electroless plating:
It uses a redox rxn. to deposit a metal on an object without the passage of electric current. It allows a constant metal ion conc. to cover all parts of the objects, it deposits metal evenly along the edges, inside the holes and over irregularly shaped objects which are difficult to plate evenly with electroplating. Electroless plating is also used to deposit a conductive surface on a non-conductive object to allow it to be electroplated.

This method involves the reduction of a complexed metal using a mild reducing agent typically HCHO . For ex- mirrors can be manufactured using this reaction.



The reaction deposits a thin coat of elemental Ag on the walls of the container.

Rochelle salt - Sod. Pot. Tartrate used in silvering of mirrors.

Lacquers - A type of clear or coloured synthetic coatings made by dissolving nitro-cellulose or other cellulose material with plasticizers and pigments.