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ROLL NO.

DATE

Dr. Jayathi C. Abbar

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## CORROSION OF METAL

### TESTS FOR CORROSION

#### Introduction to Corrosion

A vexing problem associated with every use of metal object is corrosion. Silver tarnishes; copper develops patina and iron rusts. Corrosion occurs with all metals except the least active noble metals such as gold and platinum.

Corrosion is not concerned only with metallurgists and chemists, it is now a field of interdisciplinary study as metals are universal in their use. There cannot be any field of material use which does not use metals.

The knowledge of corrosion is, therefore, of great importance to the scientific community in general, and engineers in particular. It is the engineer who plans design and constructs the final metal product for use. In this process, due importance must be given to corrosion aspect. This can be successfully done only if he knows the mechanism of corrosion & the possible methods of mechanism of control.

(Q.M)

#### Definition of Corrosion

It is defined as "the destruction or deterioration and consequent loss of metals through chemical or electrochemical attack by the environment".

Corrosion may occur either in a dry environment or in moisture.

### 1) Dry corrosion (Chemical Corrosion).

This involves direct chemical attack of metals with corrosive gases such as sulphur dioxide,  $O_2$ , ammonia, hydrogen chloride, hydrogen sulphide, etc., present in the corrosion environment. Since this is observed in the absence of moisture or conducting electrolyte, it is called as dry corrosion.

Eg:- If a metal is attacked by dry air / oxygen, metal oxide is the corrosion product.

### 2) Wet Corrosion (Electrochemical Corrosion)

If the corrosion of the metal takes place through electrochemical reaction in the presence of moisture or aqueous medium, it is called as wet corrosion.

Ex:- Dry chlorine is non-corrosive to steel but moist chlorine leads to corrosion.

#### Rusting of iron:

Wet corrosion is explained on the basis of electrochemical theory.

#### SM\* Electrochemical theory of corrosion in

According to electrochemical theory, corrosion of metals takes place due to formation of anodic and cathodic regions on the same metal surface when two different metals are in contact with each other in presence of a conducting

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medium.

When a metal such as iron is exposed to atmospheric air, the following electrochemical changes occur gradually.

a) Formation of galvanic cells:-

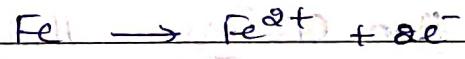
Anodic & cathodic areas are formed resulting in minute galvanic cells.

b) Anodic reaction:-

Anodic reaction is a simple oxidation reaction in which metal atoms are converted into their ions liberating electrons.

At anode region,  $M \rightarrow M^{2+} + 2e^-$

Example:- When iron undergoes corrosion,



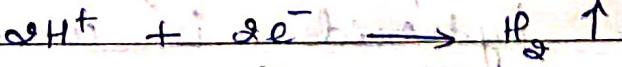
c) Cathodic reactions :- Consumes electrons either by 1) liberation of hydrogen

or 2) absorption of oxygen, depending on the nature of the corrosion environment.

If cathodic region -

i) Liberation of hydrogen takes place in the absence of oxygen.

a) In acidic medium & in the absence of oxygen, the cathodic reaction is,



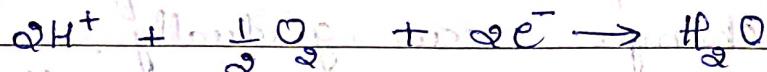
b) In neutral or alkaline medium & in the absence of oxygen, hydroxide ions are formed with simultaneous liberation of hydrogen.



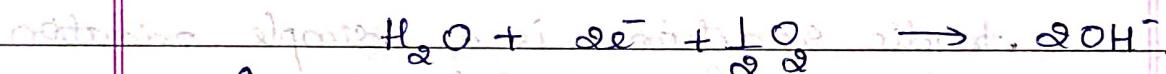
c) Absorption of oxygen takes place in the

(4) presence of oxygen.

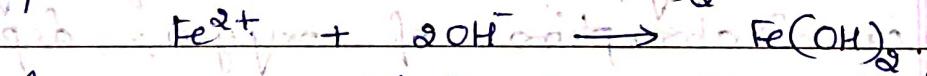
a) in acidic medium & in presence of oxygen:



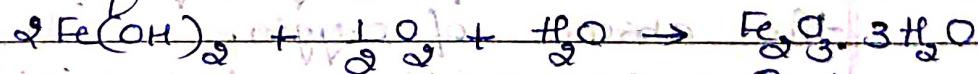
b) in neutral or alkaline medium & in the presence of oxygen, hydroxide ions are formed by the following reaction:



Corrosion of iron produces  $\text{Fe}^{2+}$  ions at anode and at cathode sites respectively. These ions diffuse towards each other. Since smaller  $\text{Fe}^{2+}$  ions diffuse more rapidly than  $\text{OH}^-$  ions their combination occurs more commonly near the cathodic region to produce insoluble  $\text{Fe(OH)}_2$ .



In an oxidising environment, it is oxidised to ferric oxide & the yellow rust is hydrated ferric oxide.



In the presence of limited oxygen, ferrous hydroxide is converted to magnetite oxide of iron ( $\text{Fe}_3\text{O}_4$ ) & is known as black rust.



[Black rust]

Magnetic oxide of rust

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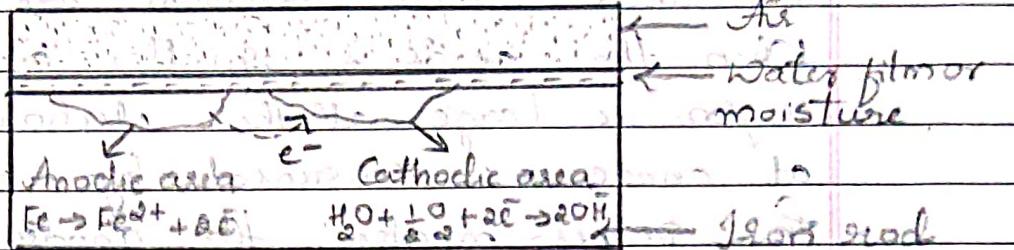
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Rusting of iron. To make iron

(5 min) \* Factors affecting the rate of corrosion:-

(5 min) Nature of the metal :- The tendency of a metal to undergo corrosion is dependent on the nature of the metal. Metals with higher electrode potential do not corrode easily.

Eg- Noble metals like gold, platinum, silver.

Whereas, metals with lower electrode potential readily undergo corrosion.

Ex- Metals like K, Na, Mg, Zn, Al etc.,

(5 min) Ratio of anodic to cathodic area:-

The rate of corrosion is greatly influenced by the relative sizes of anodic & cathodic areas. If a metal has a small anodic area & large cathodic area (ie, the ratio of anodic to cathodic area is small), then the corrosion rate at the anodic region is the highest. As the ratio decreases the corrosion rate increases rapidly.

This is explained as, at anode, oxidation takes place & electrons are liberated.

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At cathode, these electrons are consumed.

When the anode is smaller and cathode region is large, all the electrons liberated at anode are consumed by cathode region. This process makes the anodic reaction to take place at its maximum rate & thus increases corrosion rate. If the cathode is smaller, the consumption of electrons will be slower & corrosion reaction as a whole will be slower.

3) Nature of corrosion product:-

The corrosion product formed on the surface of the metal may act as protective film if it is stable, insoluble, uniform & non-porous. In case, if it acts as protective film it prevents further corrosion by acting as a barrier between metal surface & corrosion environment.

On the other hand, if corrosion product is soluble, unstable, non-uniform & porous, it further enhances corrosion.

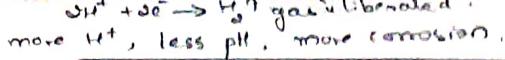
Ex- In oxidizing environment, metals like aluminium, chromium, titanium etc are highly passive as their oxides are corrosion products form protective films on the metal surfaces preventing further corrosion. Whereas metals such as iron, zinc, magnesium etc., do not form any protective film & are highly susceptible for continuous corrosion, when exposed to oxidizing environment.

$$E = E^\circ + 0.0291 \log(H^+)$$

$$\therefore E = E^\circ + 0.0291 \log(H^+)$$

$E^\circ$  dependent on  $H^+$

If  $[H^+] \uparrow$ ,  $E^\circ \downarrow$ , then difference in potential b/w cathode & anode is more.  $\therefore$  corrosion will be more.



more  $H^+$ , less pH, more corrosion.

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passivation layer

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Nature of medium :-

4) pH :-

The rate of corrosion increases with decrease in pH. At pH greater than 10, corrosion of iron practically ceases due to the formation of a protective coating of hydroxides of iron.

Between pH 10 and 3, the presence of oxygen is essential for the corrosion of iron. For example, ships submerged in deep sea water for hundreds of years remain almost unaffected.

If the pH is lower than 3, severe corrosion occurs even in the absence of air due to the continuous evolution of hydrogen at the cathodic region.

5) Conductivity :-

As the conductivity of the corrosion medium increases, corrosion rate also increases. Higher the conductivity of the medium, faster the ions can migrate between the anodic & cathodic regions of the corrosion cell, i.e. two, faster will be the exchange of electrons at the electrode surface. This facilitates the higher corrosion rate.

• Corrosion problem is more in sea water, than in fresh water.

6) Temperature :-

The rate of a chemical reaction

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(8) generally increases with increase in temperature. Corrosion process is one such chemical reaction. Rate of corrosion increases with increase in temperature. Increase in temperature increases the conductance of the corrosion medium which also contributes to the increase in corrosion rate.

In case of corrosion resistant passive metals, the rise in temperature decreases the passive range & thereby increases the corrosion rate.

- \* Types of Corrosion :-
- (i) Differential metal corrosion :- (Galvanic corrosion).

Zn	Fe	Fe	Cu
metal	metal	metal	metal

Anode Cathode Anode Cathode

This occurs when two dissimilar metals are in contact with each other in a corrosive conducting medium.

The more active metal i.e., metal with lower electrode potential acts as anode.

The less active metal i.e., metal with higher electrode potential acts as cathode.

The potential difference between the two metals is the cause or driving force for corrosion.

The anodic metal undergoes corrosion.

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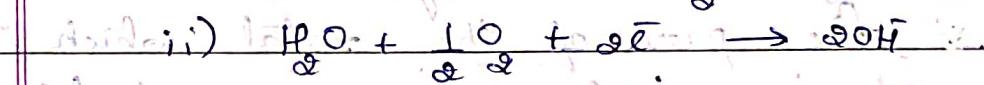
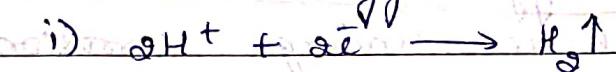
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cathodic metal is generally unaffected.

The following reactions occur during galvanic or differential metal corrosion:-



At cathode - Depending on the nature of the corrosion environment, the cathode reaction may either undergo hydrogen evolution or oxygen absorption.



Example :- i) When iron is in contact with zinc, iron acts as cathode and zinc acts as anode, because zinc has lower electrode potential compared to iron. ∴ zinc undergoes corrosion.

On the other hand, when iron is in contact with copper, iron acts as anode and undergoes corrosion, whereas copper becomes cathodic & remains unaffected.

i) Steel pipe connected to copper plumbing

ii) Steel screws in copper plating.

iv) Bolt and nut made of different metals.

v) Lead antimony solder around copper wire.

→ Uneven supply of oxygen to the areas of same metal. It is a type of electrochemical corrosion that affects metal such as steel & iron. When a poorly oxygenated area is adjacent to an area with good oxygen supply, oxidation occurs.

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CATE ROTHO  
Oxide

Differential aeration corrosion :- (Concentration Cell corrosion).

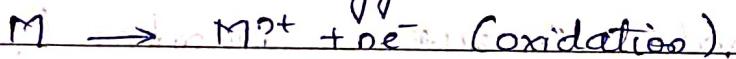
Differential aeration corrosion occurs when metal surface is exposed to different concentrations of air or oxygen.

(Ex:- Iron rod partially dipped in water).

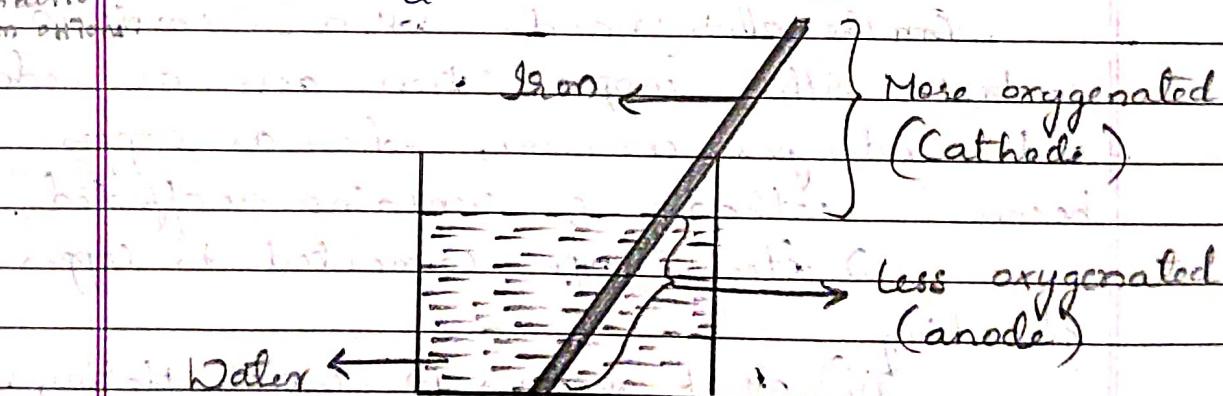
The part of the metal which is exposed to lower oxygen concentration acts as anode & hence undergoes corrosion.

The part of the metal which is exposed to higher oxygen concentration acts as cathode and hence it is unattacked.

At anode :- (less oxygenated).



At cathode :- (more oxygenated).



Some common examples are :-

- Part of nail inside the wall, being exposed to less oxygen concentration undergoes corrosion than exposed part.
- Paper pins inside the paper gets corroded and exposed part is free from corrosion.

Typical example of differential aeration

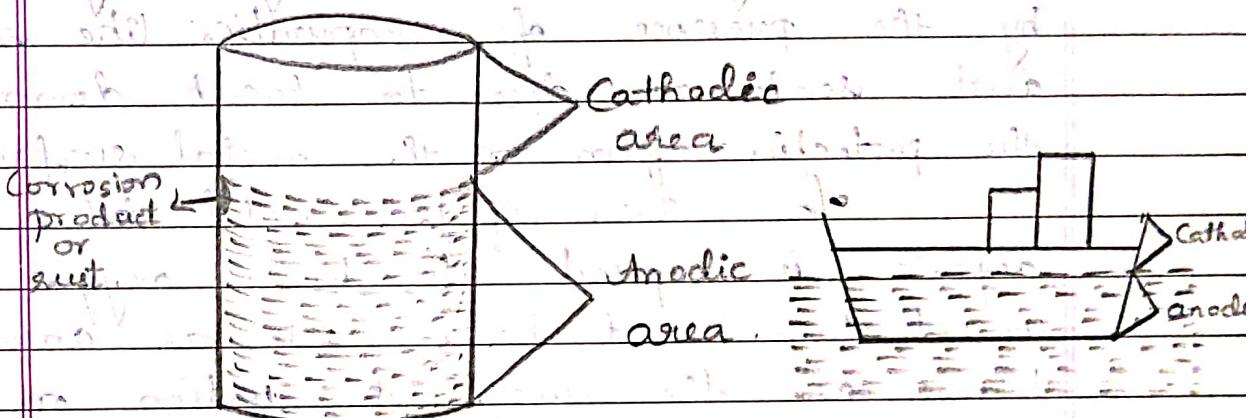
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corrosion are Waterline corrosion and Pitting Corrosion.

\* Waterline Corrosion:-

(3M) This is observed commonly in water storage steel tanks, ocean going ships etc. This takes place due to formation of oxygen concentration cell.



a) Water storage tank. b) Ocean going ship

When water is stored in a metallic tank, it is observed that corrosion takes place along the line just below the level of water in the container.

The part of the metal below the water line is exposed only to dissolved oxygen, while the part above the water is exposed to higher oxygen concentration of the atmosphere. Thus, area below water is corroded and area above water line is free from corrosion. Hence a distinct brown line is formed just below the waterline due to the deposition of rust.

This type of corrosion is also observed

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in ships floating in ocean for long period of time.

\* Pitting Corrosion :-

(3m) Pitting is one of the most destructive form of corrosion and results in the sudden failure of the equipment due to the formation of pits.

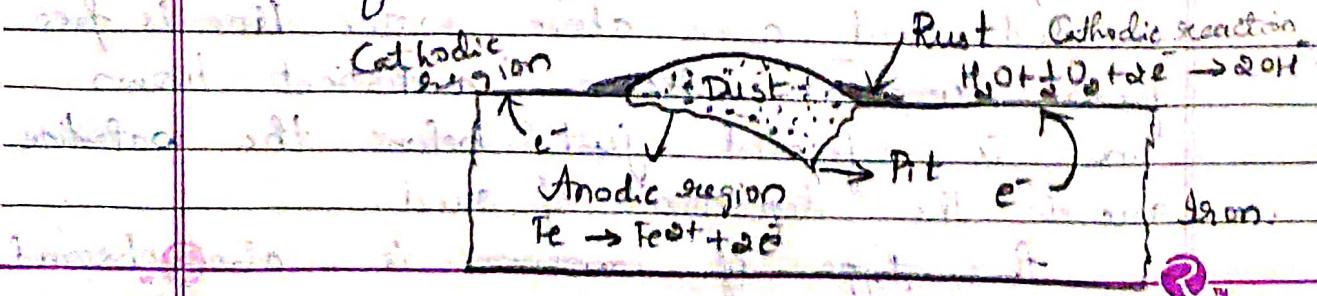
Pitting corrosion is generally initiated by the presence of impurities like sand, dust, scale or due to break down of the protective film on the metal surface.

The area of the metal below the deposit is exposed to lower oxygen concentration and hence acts as anode.

Whereas, the uncovered portion or region acts as cathode as it is exposed to higher concentration of oxygen. So, the area below the deposit undergoes corrosion leading in a pit or small hole.

Because of the small anodic & large cathodic area, corrosion becomes faster.

Once the corrosion product is formed, it further provides the condition for differential aeration below the corrosion product and as a result, pit grows and ultimately may cause failure of metal.



Cathodic protection :-

Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely to cathode.

Principle :- Metals undergo corrosion by electrochemical process with the formation of anodic and cathodic regions in contact with each other. Corrosion of metals occur at anodic region whereas,

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cathodic region is unaffected. ∴ Corrosion can be prevented by converting the entire metal into cathodic area.

This is achieved by the following metal methods,

i) Sacrificial anodic method.

ii) Impressed current method.

i) Sacrificial anodic method :-

(S.M) In this <sup>method</sup>, the metal to be protected is converted into cathode by connecting it to a more active metal. This active metal acts as an auxiliary anode.

Linc, magnesium & aluminium are the commonly used auxiliary anodes for this method. These more active metals act as anode & undergo corrosion, while the metal surface is protected. Since, the anodic metals are sacrificed to protect the metal surface structure, the method is known as sacrificial anode method.

Ex:- a) A magnesium block connected to a buried oil storage tank, acts as sacrificial anode & prevents the tank from corrosion.

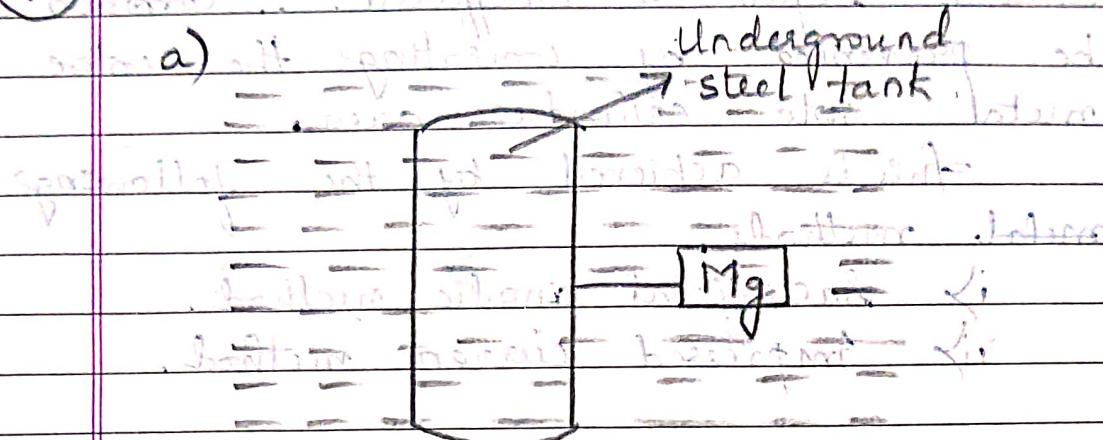
b) Magnesium blocks are connected to the sides of ship, it acts as anode, & prevents the ship from corrosion.

c) Magnesium blocks connected to buried pipe lines prevent the metal structure from corrosion, by acting as anode.

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Ques) Define cathodic protection. State its types.

Soln) a)



b)

In cathodic protection, the anode is connected to the metal which is to be protected. This anode is made of a more活泼 metal like Mg. It undergoes oxidation and electrons flow from the anode to the metal which is to be protected. Thus the metal which is to be protected remains in its reduced state.

c)

In this method, the metal which is to be protected is connected to a sacrificial anode. The sacrificial anode is made of a more活泼 metal like Mg. Electrons flow from the anode to the metal which is to be protected. Thus the metal which is to be protected remains in its reduced state.

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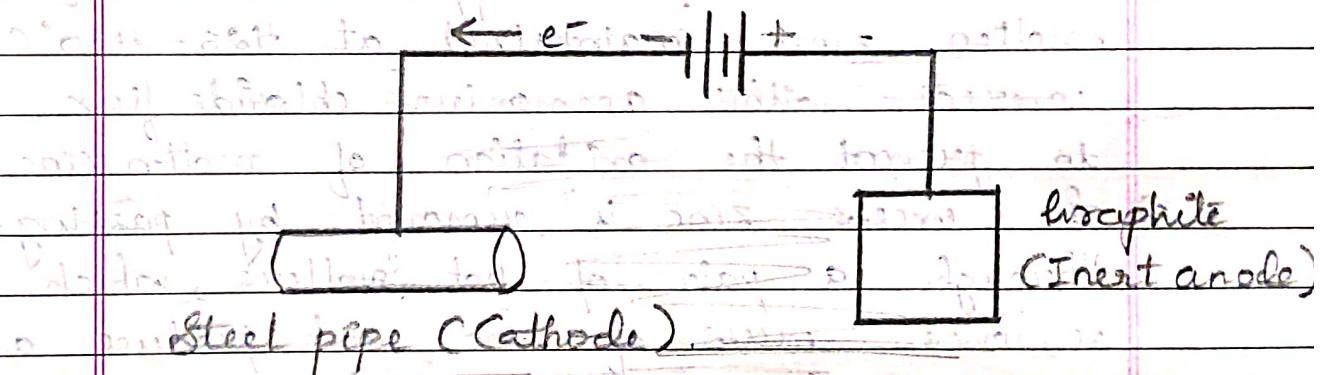
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i)

Impressed Current method :-

For this method, electrons are supplied from external source to the metallic structure which is to be protected. Metal to be protected is made cathode by connecting it to the negative terminal of DC source. A rod made up of inert graphite or platinum or silicon, is connected to the positive terminal which acts as anode.

The metal structure being cathode does not undergo corrosion, if anode being inert remains unaffected.

Steel pipe and DC source with2. Metal coatings :-

Deposition of a protective metal over the surface of a base metal (metal to be protected) is called metallic coating.

Metallic coatings are applied by electrodeposition, flame spraying, cladding, hot dipping, etc.,

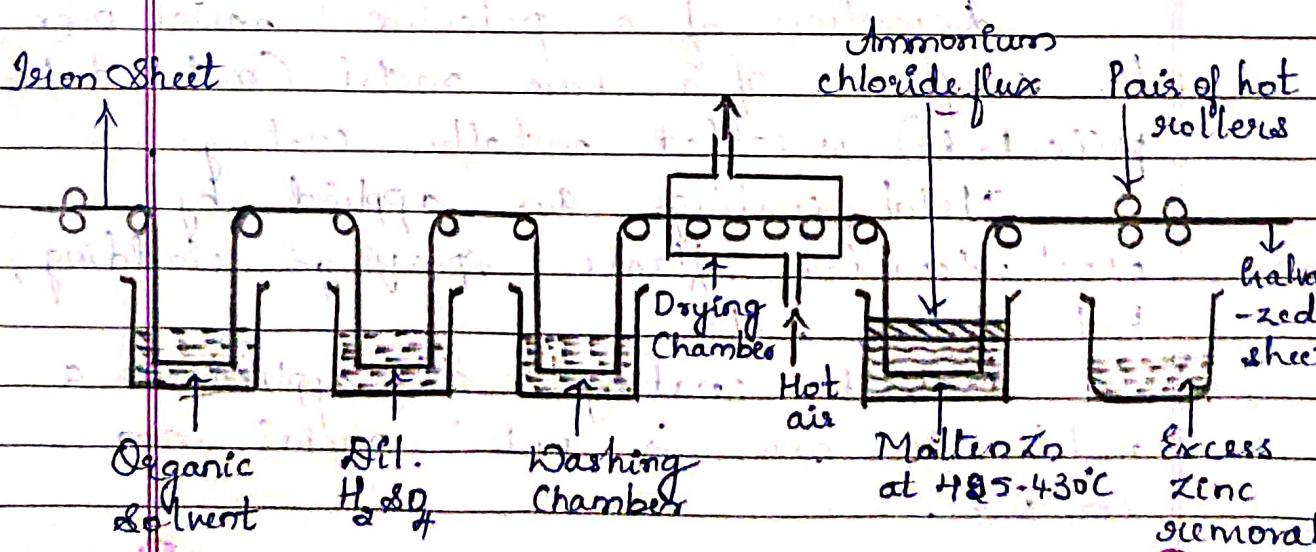
Metallic coatings are applied on a metal in order to protect metal from corrosion.

### Galvanization

(S.M.) The process of coating a base metal like steel or iron with zinc metal is called galvanization. It is carried out by hot dipping method.

It involves the following steps:

- 1) The metal surface to be galvanized is first dipped in organic solvent to remove dust or grease.
- 2) Then it is dipped in dilute sulphuric acid to remove any rust and other deposits.
- 3) Then the metal article is well washed with water and dried.
- 4) The article is then dipped in a bath of molten zinc, maintained at  $485 - 430^{\circ}\text{C}$  covered with ammonium chloride flux to prevent the oxidation of molten zinc.
- 5) The excess zinc is removed by passing through a pair of hot rollers, which removes excess of zinc and produce a thin coating of zinc coat.



Galvanization of Iron sheet. RAJDHANI

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Uses :-

It is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc.,.. Galvanized articles are however, not used for preparing and storing food stuffs, since zinc dissolves in dil. acids to form toxic zinc compounds.

Notes -

Galvanisation is an example of anodic coating. Anodic coating is the one in which the base metal is coated with more active metal which is anodic to base metal. For ex:- Iron is coated with more anodic zinc, magnesium or aluminium. The coated metal undergoes corrosion, whereas the base metal is protected.

One of the important characteristic of anodic coating is that even if the coating is ruptured the base metal does not undergo corrosion. The exposed surface of the base metal is cathodic to the coating metal & the coating metal will undergo corrosion. The protection is ensured as long as the anodic coating metal is still present on the surface. ∴ anodic coating is also known as Sacrificial coating.

(20) Table:- Galvanic Series. (in sea water)  
at 25°C & 1 atm.

Base metals:

Magnesium

Zinc

Aluminum

Cadmium

Mild steel

Cast iron

Lead

tin

Brass

Copper

Nickel

Stainless steel  
(18% Cr + 8% Ni)

Silver

Titanium

Gold

Noble metals.

Platinum.

Not for  
Syllabus.  
Just for  
Understanding.

An arrangement of metals and alloys in order of their corrosion tendencies in a corrosive environment is referred to as galvanic series.

\* to get uniform & thin deposit.

\* potassium sodium tartrate tetrahydrate  
 $\text{KNaC}_6\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$

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\* Electroless plating

(\*)

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

The reducing agent converts the metal ions ( $M^{n+}$ ) to the metal ( $M$ ) which gets plated over a catalytic surface.

$M^{n+}$  Reducing agent  $\xrightarrow{\text{Catalytic surface}}$   $M + \text{Oxidised product}$ .  
 The driving force in electroless plating is an autocatalytic redox reaction on a pretreated active surface.

\*

Composition of an Electroless plating bath:-

1) Ni, 2)  $\text{NiCl}_2$

3) Cu, 4) Salt of Cu.

5)  $\text{CuSO}_4$ .

6) To improve quality of the deposit.

It source of electro active metal in the form of a soluble salt. Ex:-  $\text{NiCl}_2$ ,  $\text{CuSO}_4$ .

Reducing agent to reduce metal ions to metal atoms. Ex:- Sodium hypophosphite, formaldehyde (then gets oxidising supply to the  $M^{n+}$  to form  $M$ )

Complexing agents to form complex compounds with metal ions. Ex:- EDTA, Sodium Succinate.

Accelerators to increase rate of plating.

Stabilizers to give more stability to solution.

• Buffer to control pH. Ex:- Sodium hydroxide + Rochelle salt.

\*

Surface Preparation:-

1) Acid treatment (etching).

2) Electroplating a thin layer of the metal same as that of the to be plated or

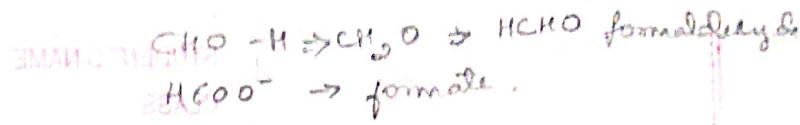
Reducing agent gets oxidised to release e's, & these e's are taken by Ni<sup>++</sup>

$\text{H}_2\text{PO}_4^- \rightarrow$  dit hydrogen phosphate

$\text{H}_2\text{PO}_3^- \rightarrow$  hypophosphate

another suitable metal) followed by heat treatment. (to improve coating's catalytically active).

3. For non-conducting surfaces such as plastics or painted circuit boards, the surface is treated with SnCl<sub>4</sub> and Palladium chloride solution alternately.



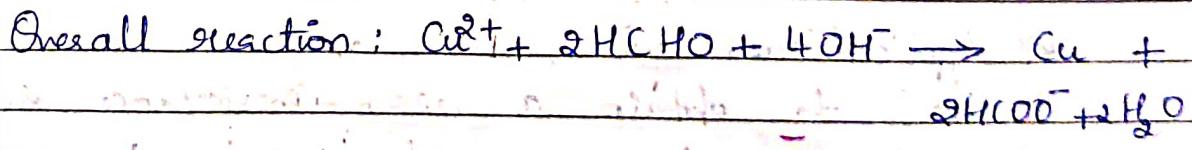
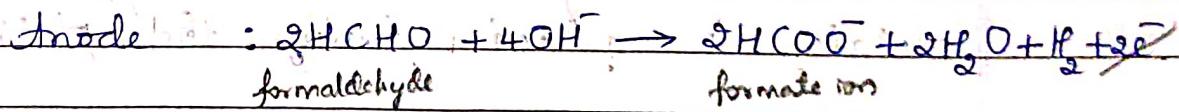
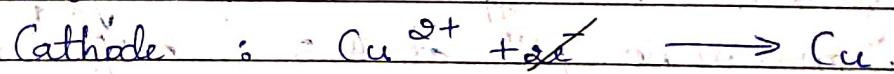
## ✓ \* Electroless plating of Copper:

Before electrodes plating the surface is cleaned thoroughly. Insulators such as plastics & printed circuit boards are activated by dipping first in  $\text{SnCl}_4$  <sup>containing HCl at 25%</sup> then in palladium chloride ( $\text{PdCl}_2$ ).

Then the electrodes plating is done under the following conditions:-

<p>Plating bath solution          (explain in one line about each component)</p>	<p>Solution of Copper sulphate (12 g per L).</p>
<p>Reducing agent,</p>	<p>Formaldehyde (8 g per L).</p>
<p>Complexing agent &amp; exaltant</p>	<p>&amp; EDTA (20 g/L).</p>
<p>Buffer (pH = 11),</p>	<p>Sodium hydroxide (15 g/L)</p>
<p>pH</p>	<p>11</p>
<p>Temperature</p>	<p>25 °C</p>

## Reactions :-



Formaldehyde & Copper sulphate are added to the plating bath periodically.

\* Application :- 2) through hole connections in PCB's -  
typical application of Electroless copper is  
Printed Circuit boards (PCBs), particularly  
double sided boards in which plating

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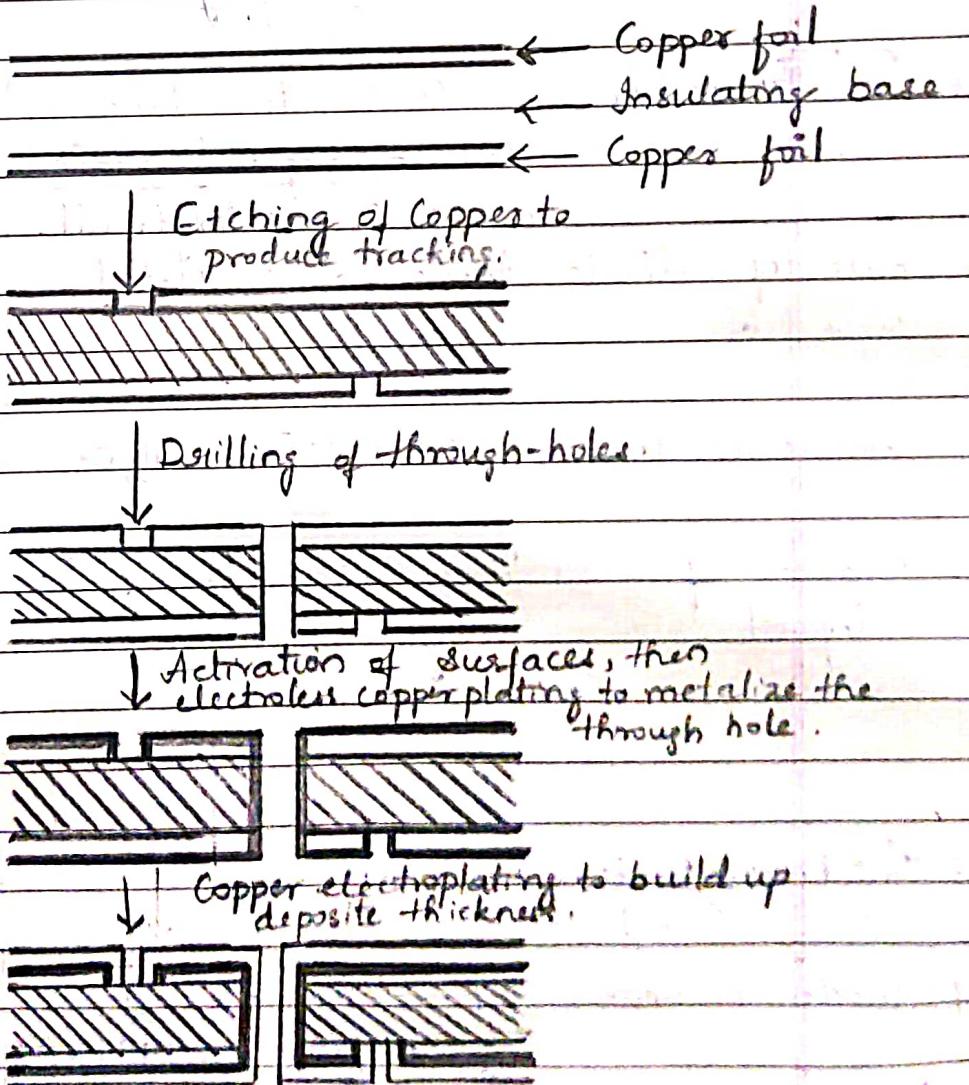
Through hole is required.

The two sides of a plastic board is initially covered with copper layers by cladding thin layers of electroformed copper foil.

Selected areas are protected & the remaining areas are etched away to produce tracking on both the sides.

The connection between two sides is made by drilling hole followed by activation & plating through holes by electrodeless plating.

The steps involved in the process are shown below,



- 3) For plating of non-conductors.
- 4) As a base for subsequent conventional electroplating.
- 5) Applied on wave guides and for decorative plating on plastics.

(6m) \* Distinction between Electroplating and Electroless plating processes is

Property	Electroplating	Electroless plating.
1. Driving force	Electrical energy is obtained from external source. i.e., Power supply	Electrical energy not required. i.e., Autocatalytic redox reaction.
2. Site of Anode reaction	Anode reaction takes place at <u>separate anode</u> used in the electrolytic cell.	The site of anode reaction is the article to be plated
3. Site of cathode reaction	Article to be plated	Catalytic surface of the article to be plated.
4. Anode reactant	Metal (M) or $H_2O$ .	Reducing agent in solution.
5. Nature of deposit.	Pure metal or definite alloy.	Contaminated i.e., usually metal contaminated with reducing agent - desired species.
6. Thickness limit (μm)	1-100	1-100.
7. Anode reaction	$M \rightarrow M^{n+} + n\bar{e}$ OR $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2\bar{e}$	Reducing agent $\rightarrow$ Oxidised product + $n\bar{e}$
8. Cathode reaction	$M^{n+} + n\bar{e} \rightarrow M$	$M^{n+} + n\bar{e} \rightarrow M$
9. Applicability.	Only to Conductors	Conductors & non-conductors