

CORROSION ENGINEERING

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INTRODUCTION:

Corrosion is an undesirable process. Due to corrosion there is limitation of progress in many areas. The cost of replacement of materials and equipments lost through corrosion is unlimited.

Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of destruction of metals and alloys is known as corrosion.

Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interactions with the environment. Thus, it is exactly the reverse of extraction of metals from ores.

Example: Rusting of iron

A layer of reddish scale and powder of oxide (Fe_3O_4) is formed on the surface of iron metal.

A green film of basic carbonate [$\text{CuCO}_3 + \text{Cu}(\text{OH})_2$] is formed on the surface of copper, when it is exposed to moist -air containing carbon dioxide.

CONSEQUENCES (EFFECTS) OF CORROSION:

The economic and social consequences of corrosion include

- i) Due to formation of corrosion product over the machinery, the efficiency of the machine gets failure leads to plant shut down.
- ii) The products contamination or loss of products due to corrosion.
- iii) The corroded equipment must be replaced
- iv) Preventive maintenance like metallic coating or organic coating is required.
- v) Corrosion releases the toxic products.
- vi) Health (eg., from pollution due to a corrosion product or due to the escaping chemical from a corroded equipment).

CAUSES OF CORROSION:

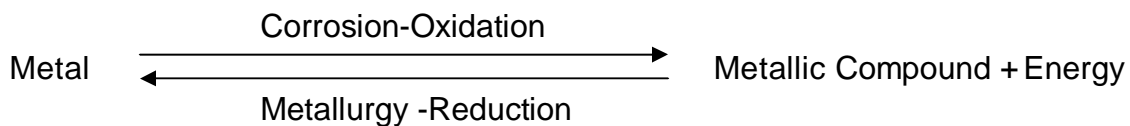
In nature, metals occur in two different forms.

- 1) Native State
- (2) Combined State

Native State: The metals exist as such in the earth crust then the metals are present in a native state. Native state means free or uncombined state. These metals are non-reactive in nature. They are noble metals which have very good corrosion resistance. Example: Au, Pt, Ag, etc.,

Combined State: Except noble metals, all other metals are highly reactive in nature which undergoes reaction with their environment to form stable compounds called ores and minerals. This is the combined state of metals. Example: Fe₂O₃, ZnO, PbS, CaCO₃, etc.,

Metallic Corrosion: The metals are extracted from their metallic compounds (ores). During the extraction, ores are reduced to their metallic states by applying energy in the form of various processes. In the pure metallic state, the metals are unstable as they are considered in excited state (higher energy state). Therefore as soon as the metals are extracted from their ores, the reverse process begins and form metallic compounds, which are thermodynamically stable (lower energy state). Hence, when metals are used in various forms, they are exposed to environment, the exposed metal surface begin to decay (conversion to more stable compound). This is the basic reason for metallic corrosion.



Although corroded metal is thermodynamically more stable than pure metal but due to corrosion, useful properties of a metal like malleability, ductility, hardness, luster and electrical conductivity are lost.

CLASSIFICATION OR THEORIES OF CORROSION

Based on the environment, corrosion is classified into

- (i) Dry or Chemical Corrosion
- (ii) Wet or Electrochemical Corrosion

DRY or CHEMICAL CORROSION:

This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid, etc. The chemical corrosion is defined as the direct chemical attack of metals by the atmospheric gases present in the environment.

- Example: (i) Silver materials undergo chemical corrosion by Atmospheric H₂S gas .
(ii) Iron metal undergo chemical corrosion by HCl gas.

TYPES OF DRY or CHEMICAL CORROSION:

1. Corrosion by Oxygen or Oxidation corrosion
2. Corrosion by Hydrogen
3. Liquid Metal Corrosion

CORROSION BY OXYGEN or OXIDATION CORROSION:

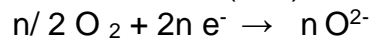
Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K et c.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized. The reactions of oxidation corrosion are as follows:

Mechanism:

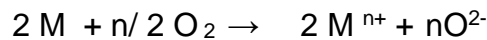
- 1) Oxidation takes place at the surface of the metal forming metal ions M^{2+}



- 2) Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.



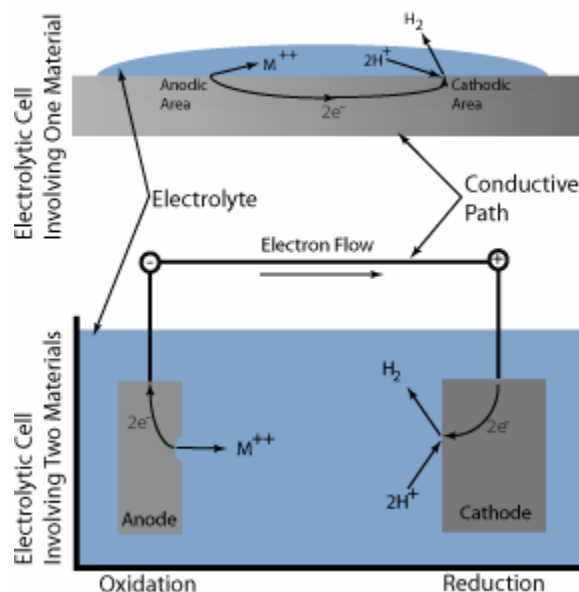
- 3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.



The Nature of the Oxide formed plays an important part in oxidation corrosion process.



When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is



(i) Stable layer:

A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such layer can be of impervious nature (ie., which cuts -off penetration of attaching oxygen to the underlying metal). Such a film behaves as protective coating in nature, thereby shielding the metal surface. The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable, tightly adhering and impervious in nature.

(ii) Unstable oxide layer:

This is formed on the surface of noble metals such as Ag, Au, Pt. As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

(iii) Volatile oxide layer:

The oxide layer film volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. MoO_3 is volatile in nature.

(iv) Porous layer:

The layer having pores or cracks. In such a case, the atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

Pilling-Bedworth rule: According to it “an oxide is protective or non -porous, if the volume of the oxide is atleast as great as 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 metal, the oxide layer is porous (or non-continuous) and hence, non-protective, because it cannot prevent the access of oxygen to the fresh metal surface below”.

Thus, alkali and alkaline earth metals (like Li, K, Na, Mg) form oxides of volume less than the volume of metals. Consequently, the oxide layer faces stress and strains, thereby developing cracks and pores in its structure. Porous oxide scale permits free access of oxygen to the underlying metal surface (through cracks and pores) for fresh action and thus, corrosion continues non-stop.

Metals like Aluminium forms oxide, whose volume is greater than the volume of metal. Consequently, an extremely tightly -adhering non-porous layer is formed. Due to the absence of any pores or cracks in the oxide film, the rate of oxidation rapidly decreases to zero.

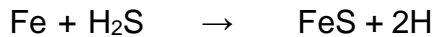
Corrosion by other gases (by hydrogen):

1) Hydrogen Embrittlement:

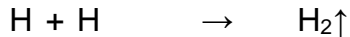
Loss in ductility of a material in the presence of hydrogen is known as hydrogen embrittlement .

Mechanism:

This type of corrosion occurs when a metal is exposed to hydrogen environment. Iron liberates atomic hydrogen with hydrogen sulphide in the following way.



Hydrogen diffuses into the metal matrix in this atomic form and gets collected in the voids present inside the metal. Further, diffusion of atomic hydrogen makes them combine with each other and forms hydrogen gas.



Collection of these gases in the voids develops very high pressure, causing cracking or blistering of metal.

2) Decarburisation:

The presence of carbon in steel gives sufficient strength to it. But when steel is exposed to hydrogen environment at high temperature, atomic hydrogen is formed.



Atomic hydrogen reacts with the carbon of the steel and produces methane gas.



Hence, the carbon content in steel decreases. The process of decrease in carbon content in steel is known as decarburization.

Collection of methane gas in the voids of steel develops high pressure, which causes cracking. Thus, steel loses its strength.

3) Liquid metal corrosion:

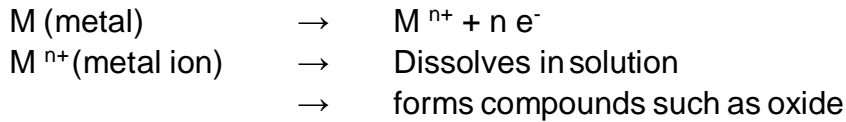
This is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occurs in devices used for nuclear power. The corrosion reaction involves either: (i) dissolution of a solid metal by a liquid metal or (ii) internal penetration of the liquid metal into the solid metal. Both these modes of corrosion cause weakening of the solid metal.

WET OR ELECTROCHEMICAL CORROSION

Electrochemical corrosion involves:

- i) The formation of anodic and cathodic areas or parts in contact with each other
- ii) Presence of a conducting medium
- iii) Corrosion of anodic areas only and
- iv) Formation of corrosion product somewhere between anodic and cathodic areas. This involves flow of electron -current between the anodic and cathodic areas.

At anodic area oxidation reaction takes place (liberation of free electron), so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide, etc.). Hence corrosion always occurs at a nodic areas.



At cathodic area, reduction reaction takes place (gain of electrons), usually cathode reactions do not affect the cathode, since most metals cannot be further reduced. So at cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions like OH⁻ and O₂⁻.

Cathodic reaction consumes electrons with either by

- (a) evolution of hydrogen or
- (b) absorption of oxygen, depending on the nature of the corrosive environment

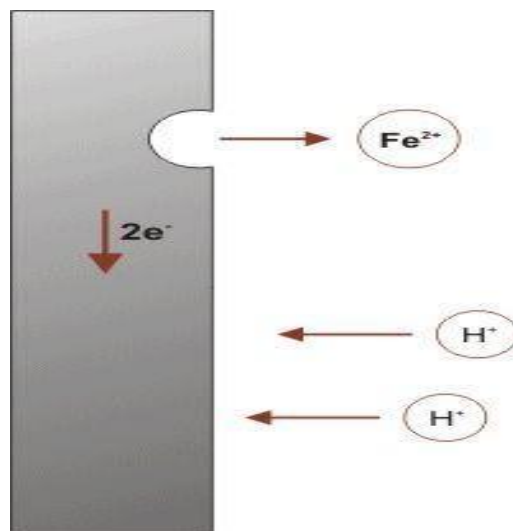
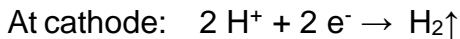
Hydrogen Evolution Type:

All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

It occurs in acidic environment. Consider the example of iron



These electrons flow through the metal, from anode to cathode, where H⁺ ions of acidic solution are eliminated as hydrogen gas.



Oxygen Absorption Type:

Rusting of iron in neutral aqueous solution of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is usually coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts acts as cathodes.

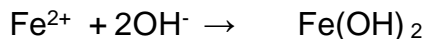
At Anode: Metal dissolves as ferrous ions with liberation of electrons.



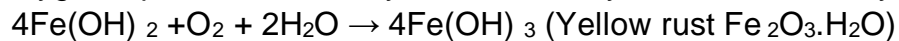
At Cathode: The liberated electrons are intercepted by the dissolved oxygen.



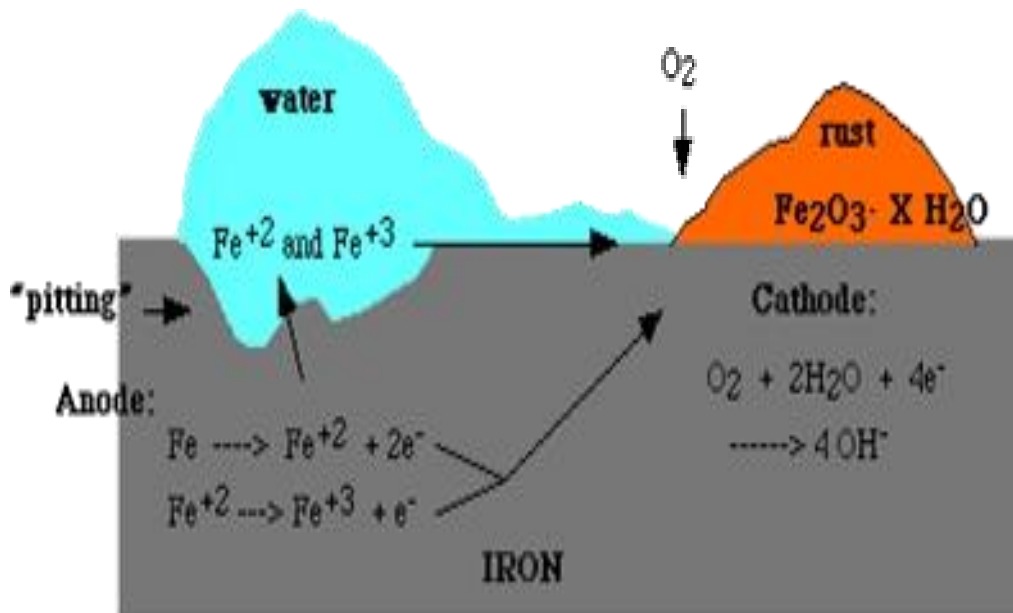
The Fe^{2+} ions and OH^{-} ions diffuse and when they meet, ferrous hydroxide is precipitated.



(i) If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.



(ii) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe_3O_4 .



Difference between (dry) chemical and (wet) electrochemical corrosion:

Sl. No.	Chemical Corrosion	Electrochemical Corrosion
1.	It occurs in dry condition.	It occurs in the presence of moisture or electrolyte.
2.	It is due to the direct chemical attack of the metal by the environment.	It is due to the formation of a large number of anodic and cathodic areas.
3.	Even a homogeneous metal surface gets corroded.	Heterogeneous (bimetallic) surface alone gets corroded.
4.	Corrosion products accumulate at the place of corrosion	Corrosion occurs at the anode while the products are formed elsewhere.
5.	It is a self controlled process.	It is a continuous process.
6.	It adopts adsorption mechanism.	It follows electrochemical reaction.
7.	Formation of mild scale on iron surface is an example.	Rusting of iron in moist atmosphere is an example.

TYPES OF ELECTROCHEMICAL CORROSION

The electrochemical corrosion is classified into the following two types:

- (i) Galvanic (or Bimetallic) Corrosion
- (ii) Differential aeration or concentration cell corrosion.

Galvanic Corrosion:

When two dissimilar metals (eg., zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. In this process, the more active metal (with more negative electrode potential) acts as an anode while the less active metal (with less negative electrode potential) acts as cathode.

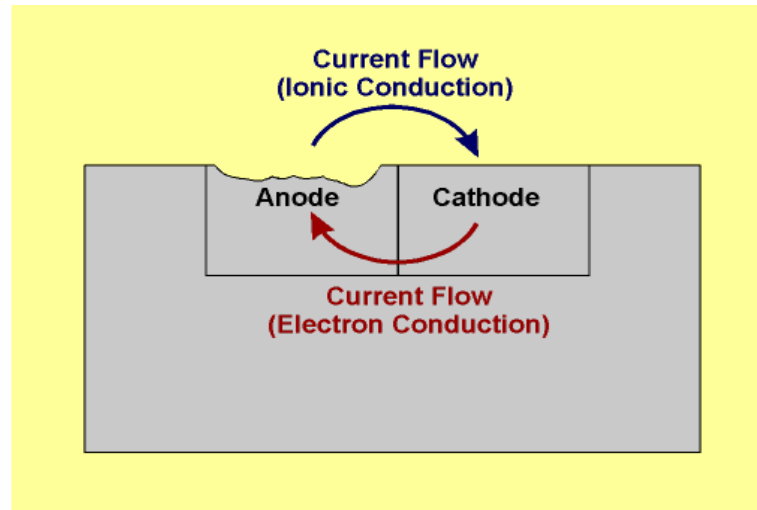
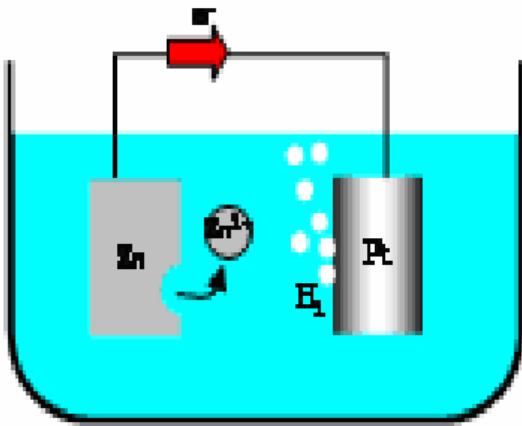
In the above example, zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series or more noble) acts as cathode.

Mechanism: In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron current flows from the anode metal, zinc to the cathode metal, copper.



Thus it is evident that the corrosion occurs at the anode metal; while the cathodic part is protected from the attack.

Example: (i) Steel screws in a brass marine hardware (ii) Lead-antimony solder around copper wire; (iii) a steel propeller shaft in bronze bearing (iv) Steel pipe connected to copper plumbing.



Concentration Cell Corrosion:

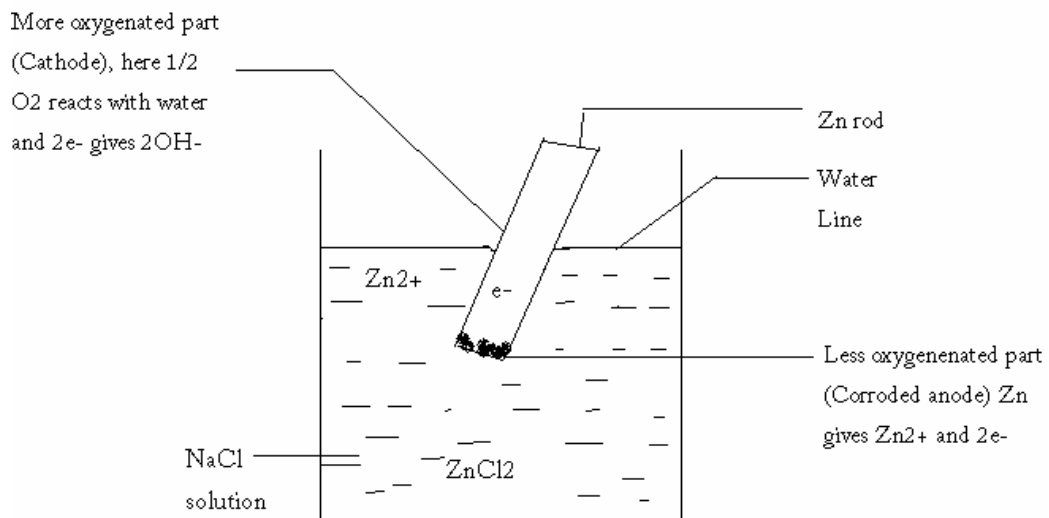
It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration.

It occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that poor -oxygenated parts are anodic.

Examples: i) The metal part immersed in water or in a conducting liquid is called water line corrosion.

ii) The metal part partially buried in soil.

Explanation: If a metal is partially immersed in a conducting solution the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated and thus becomes anodic and suffers corrosion.



At anode: Corrosion occurs (less aerated) $M \longrightarrow M^{2+} + 2e^{-}$

At cathode: OH⁻ ions are produced (more aerated) $\frac{1}{2} O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-}$

Examples for this type of corrosion are

- 1) Pitting or localized corrosion
- 2) Crevice corrosion
- 3) Pipeline corrosion
- 4) Corrosion on wire fence

Pitting Corrosion:

Pitting is a localized attack, which results in the formation of a hole around which the metal is relatively unattacked.

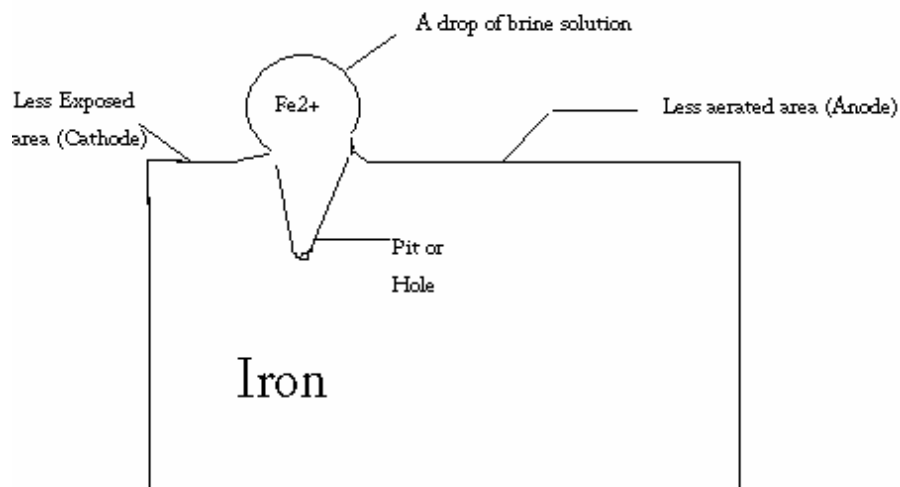
The mechanism of this corrosion involves setting up of differential aeration or concentration cell.

Metal area covered by a drop of water, dust, sand, scale etc. is the aeration or concentration cell.

Pitting corrosion is explained by considering a drop of water or brine solution (aqueous solution of NaCl) on a metal surface, (especially iron).

The area covered by the drop of salt solution as less oxygen and acts as anode. This area suffers corrosion, the uncovered area acts as cathode due to high oxygen content.

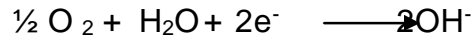
It has been found that the rate of corrosion will be more when the area of cathode is larger and the area of the anode is smaller. Hence there is more material around the small anodic area results in the formation hole or pit.



At anode: Fe is oxidized to Fe²⁺ and releases electrons.



At cathode: Oxygen is converted to hydroxide ion

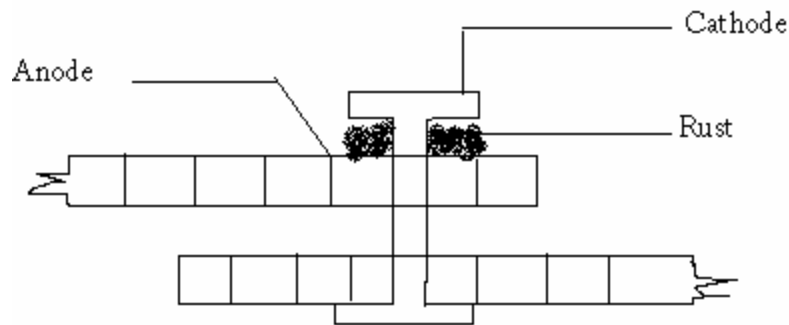


The net reaction is $\text{Fe} + 2\text{OH}^{-} \longrightarrow \text{Fe}(\text{OH})_2$

The above mechanisms can be confirmed by using ferroxyl indicator (a mixture containing phenolphthalein and potassium ferricyanide). Since OH⁻ ions are formed at the cathode, this area imparts pink colour with phenolphthalein indicator. At the anode, iron is oxidized to Fe²⁺ which combines with ferricyanide and shows blue colour.

Crevice corrosion:

If a crevice (a crack forming a narrow opening) between metallic and non-metallic material is in contact with a liquid, the crevice becomes anodic region and undergoes corrosion. Hence, oxygen supply to the crevice is less. The exposed area has high oxygen supply and acts as cathode.



Crevice Corrosion

Bolts, nuts, rivets, joints are examples for this type of corrosion.

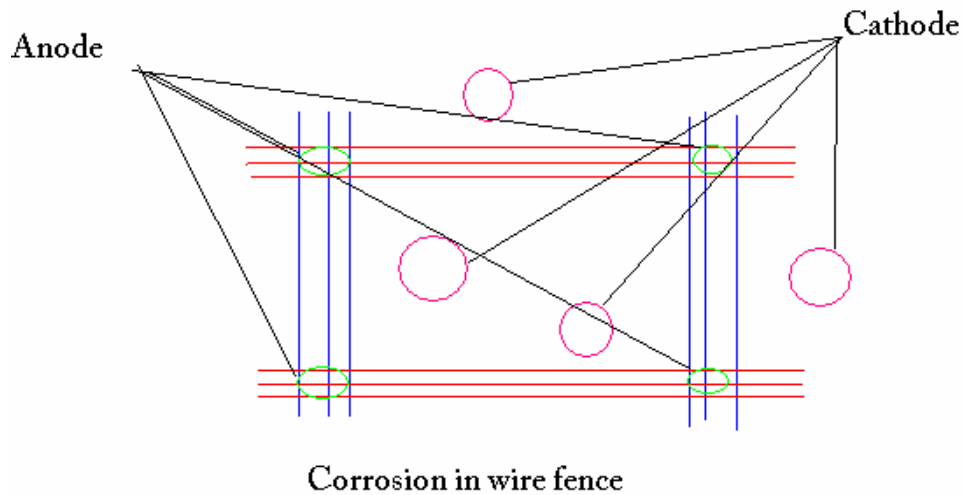
Pipeline corrosion:

Buried pipelines or cables passing from one type of soil (clay less aerated) to another soil (sand more aerated) may get corroded due to differential aeration.

Corrosion in wire fence:

A wire fence is one in which the areas where the wires cross (anodic) are less aerated than the rest of the fence (cathodic). Hence corrosion takes place at the wire crossing.

Corrosion occurring under metal washers and lead pipeline passing through clay to cinders(ash) are other examples.



FACTORS INFLUENCING CORROSION

There are two factors that influence the rate of corrosion. Hence a knowledge of these factors and the mechanism with which they affect the corrosion rate is essential because the rate of corrosion is different in different atmosphere.

1. Nature of the metal

2. Nature of the corroding environment

Nature of the metal:

- a) **Physical state:** The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc). The smaller the grain size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.
- b) **Purity of metal:** Impurities in a metal cause heterogeneity and form minute/ tiny electrochemical cells (at the exposed parts), and the anodic parts get corroded. The cent percent pure metal will not undergo any type of corrosion. For example, the rate of corrosion of aluminium in hydrochloric acid with increase in the percentage impurity is noted.

% purity of aluminium	99.99	99.97	99.2
Relative rate of corrosion	1	1000	30000

- c) **Over voltage:** The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate. For example, the over voltage of hydrogen is 0.7 v when zinc metal is placed in 1 M sulphuric acid and the rate of corrosion is low. When we add small amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33 V. This results in the increased rate of corrosion of zinc metal.

- d) **Nature of surface film:** In aerated atmosphere, practically all metals get covered with a thin surface film (thickness=a few angstroms) of metal oxide. The ratio of the volumes of the metal oxide to the metal is known as a specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. The specific volume ratios of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively. Consequently the rate of oxidation of tungsten is least, even at elevated temperatures..
- e) **Relative areas of the anodic and cathodic parts:** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.

Corrosion is more rapid and severe, and highly localized, if the anodic area is small (eg., a small steel pipe fitted in a large copper tank) , because the current density at a smaller anodic area is much greater and the demand for electrons can be met by smaller anodic areas only by undergoing corrosion more briskly.

- f) **Position in galvanic series:**
 g) **Passive character of metal :**
 h) **Solubility of corrosion products:**
 i) **Volatility of corrosion products :**

Nature of the Corroding Environment:

- a) **Temperature:** The rate of corrosion is directly proportional to temperature i.e., rise in temperature increases the rate of corrosion. This is because the rate of diffusion of ions increases with rise in temperature.
- b) **Humidity of air:** The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide etc. in the air to produce the electrolyte which is required for setting up a corrosion cell.
- c) **Presence of impurities in atmosphere:** Atmosphere in industrial areas contains corrosive gases like CO₂, H₂S, SO₂ and fumes of HCl, H₂SO₄ etc. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.
- d) **Presence of suspended particles in atmosphere:** In case of atmospheric corrosion: (i) if the suspended particles are chemically active in nature (like NaCl, Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion; (ii) if the suspended particles are chemically inactive in nature (eg., charcoal), they absorb both sulphur gases and moisture and slowly enhance corrosion rate.
- e) **Influence of pH:** Generally acidic media (i.e., pH<7) are more corrosive than alkaline and neutral media. However, amphoteric metals (like Al, Zn, Pb, etc.) dissolve in alkaline solutions as complex ions. The corrosion rate of iron in oxygen-free water is slow, until the pH is below 5. The corresponding corrosion rate in presence of oxygen is much higher. Consequently corrosion of metals, readily attacked by acid, can be reduced by

increasing the pH of the attacking environment, eg., Zn (which is rapidly corroded, even in weakly acidic solutions such as carbonic acid suffers minimum corrosion at pH=11.

- f) Nature of ions present:
- g) Conductance of the corroding medium :
- h) Formation of oxygen concentration cell :
- i) Flow velocity of process stream :
- j) Polarization of electrodes :

CORROSION CONTROL (PROTECTION AGAINST CORROSION)

As the corrosion process is very harmful and losses incurred are tremendous, it becomes necessary to minimize or control corrosion of metals. Corrosion can be stopped completely only under ideal conditions. But the attainment of ideal conditions is not possible. However, it is possible only to minimize corrosion considerably. Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so different, diverse methods are used to control corrosion. As the corrosion is a reaction between the metal or alloy and the environment, any method of corrosion control must be aimed at either modifying the metal or the environment.

a. Choice of metals and alloys:

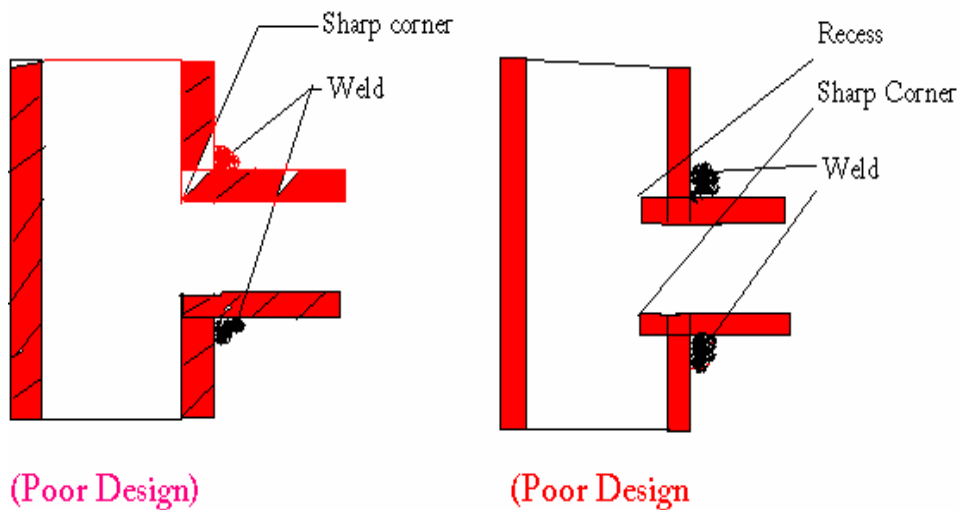
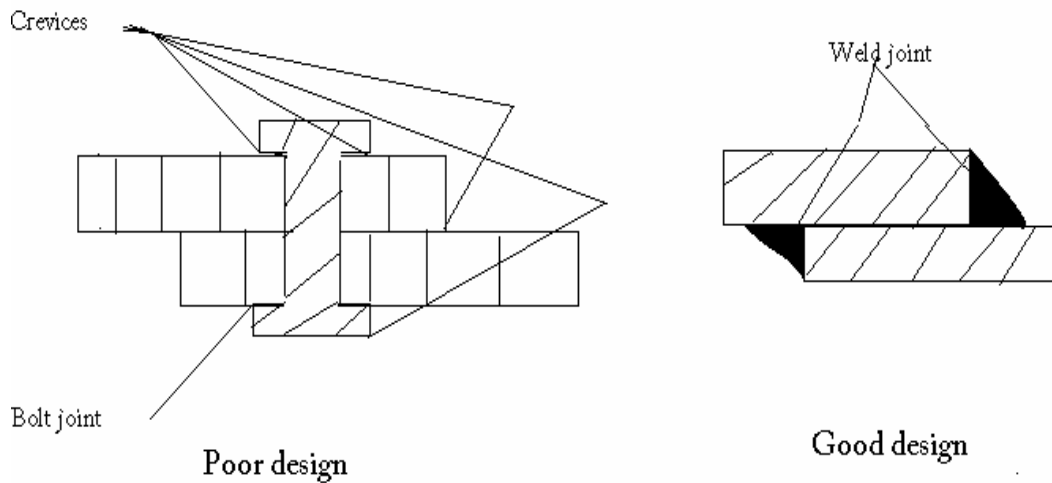
1. The first choice is to use noble metals such as gold and platinum. They are most resistant to corrosion. As they are precious, they cannot be used for general purposes.
2. The next choice is to use purest possible metal. But in many cases, it is not possible to produce a metal of high chemical purity. Hence, even a trace amount of impurity leads to corrosion.
3. Thus, the next choice is the use of corrosion resistant alloys. Several corrosion resistant alloys have been developed for specific purposes and environment. For example, a) Stainless steel containing chromium produce an exceptionally coherent oxide film which protects the steel from further attack. (b) Cupro-nickel (70% Cu + 30%Ni) alloys are now used for condenser tubes and for bubble trays used in fractionating column in oil refineries. (c) Highly stressed Nimonic alloys (Ni-Cr-Mo alloys) used in gas turbines are very resistant to hot gases.

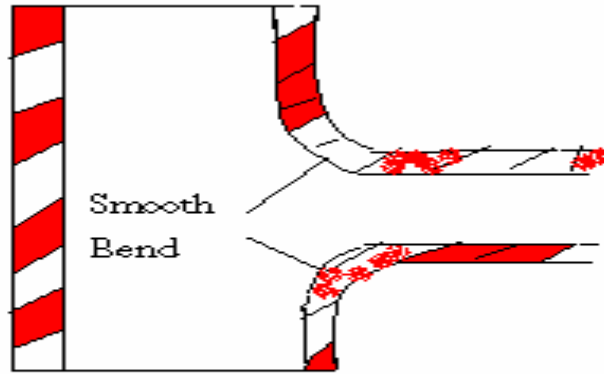
b. Proper Designing:

Proper geometrical design plays a vital role in the control of corrosion of equipments and structures. The general guidelines of the design of materials and components to control corrosion are the following:

- a. Use always simple design and structure
- b. The design must avoid more complicated shapes having more angles, edges, corners etc.
- c. Avoid the contact of dissimilar metals as they may lead to galvanic type corrosion. To overcome this, insulation can be used.

- d. When two dissimilar metals are to be in contact, the anodic area must be as large as possible and the cathodic area should be as small as possible.
- e. As far as possible, crevices (gap or crack) should be avoided between adjacent parts of a structure.
- f. Bolts and rivets should be replaced by proper welding
- g. Metal washers should be replaced by rubber or plastic washers as they do not adsorb water. They also act as insulation.
- h. Corrosion in pipelines can be prevented by using smooth bends.
- i. Heat treatment like annealing minimizes the stress corrosion.
- j. A good design of water storage container is the one from which water can be drained and cleaned easily. Such a design avoids accumulation of dirt etc.





(Best Design)

CATHODIC PROTECTION:

The reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell is called cathodic protection. Since there will not be any anodic area on the metal, corrosion does not occur. There are two methods of applying cathodic protection to metallic structures.

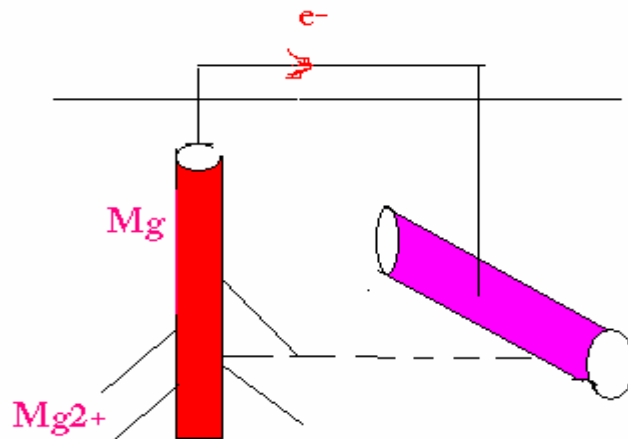
- a) Sacrificial anodic protection (galvanic protection)
- b) Impressed current cathodic protection

SACRIFICIAL ANODIC PROTECTION METHOD

In this method, the metallic structure to be protected is made cathode by connection it with more active metal (anodic metal). Hence, all the corrosion will concentrate only on the active metal. The parent structure is thus protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Magnesium has the most negative potential and can provide highest current output and hence is widely used in high resistivity electrolytes like soil.

Applications:

1. Protection as buried pipelines, underground cables from soil corrosion.
2. Protection from marine corrosion of cables, ship hulls, piers etc.
3. Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.
4. Calcium metal is employed to minimize engine corrosion.



In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (eg., a pipeline, bridge, ship hull or boat).

Advantages:

1. Low installation and operating co st.
2. Capacity to protect complex structures.
3. Applied to wide range of severe corrodents.

Limitations:

1. High starting current is required.
2. Uncoated parts cannot be protected.
3. Limited driving potential, hence , not applicable for large objects.

IMPRESSED CURRENT CATHODIC PROTECTION METHOD

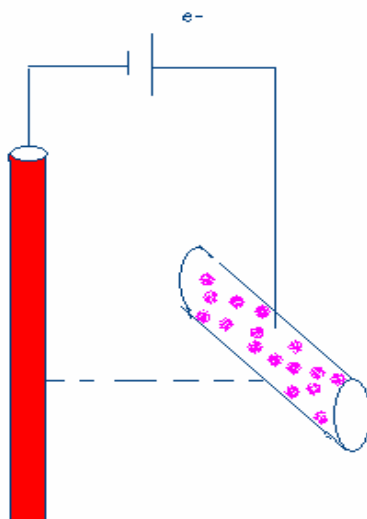
In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

Usually the impressed current is derived from a direct current sources (like battery or rectifier on AC line) with an insoluble, inert anode (like graphite, scrap iron, stainless steel, platinum or high silica iron).

A sufficient DC current is applied to an inert anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is, usually, a back fill, composed of coke breeze or gypsum, so as to increase the electrical contact with the surrounding soil.

Impressed current cathodic protection has been applied to open water box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid up ships etc.

This kind of protection technique is particularly useful for large structures for long term operations.



In Impressed-current cathodic protection, electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized.

Comparison of Sacrificial anode method with Impressed current cathodic method:

Sl. No.	Sacrificial Anode method	Impressed Current method
1/	External power supply is not required.	External power supply is required.
2/	The cost of investment is low.	The cost of investment is high.
3/	This requires periodic replacement of sacrificial anode.	Replacement is not required as anodes are stable.
4/	Soil and microbiological corrosion effects are not considered.	Soil and microbiological corrosion effects are taken into account.
5/	This is the most economical method especially when short term protection is required.	This is well suited for large structures and long term operations.
6/	This is a suitable method when the current requirement and the resistivity of the electrolytes are relatively low.	This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.

MODIFYING THE ENVIRONMENT -CORROSION CONTROL

Environment plays a major role in the corrosion of metals. Hence, we can prevent corrosion to a great extent by modifying the environment. Some of the methods are

i) Deaeration:

Fresh water contains dissolved oxygen. The presence of increased amount of oxygen is harmful and increases the corrosion rate. Deaeration involves the removal of dissolved oxygen by increase of temperature together with mechanical agitation. It also removes dissolved carbon dioxide in water

ii) By using inhibitors:

Inhibitors are organic or inorganic substances which decrease the rate of corrosion. Usually the inhibitors are added in small quantities to the corrosive medium. Inhibitors are classified into

- 1) Anodic inhibitors (chemical passivators)
- 2) Cathodic inhibitors (adsorption inhibitors)
- 3) Vapour phase inhibitors (volatile corrosion inhibitors)

Anodic Inhibitors:

Inhibitors which retard the corrosion of metals by forming a sparingly soluble compound with a newly produced metal cations. This compound will then adsorb on the corroding metal surface forming a passive film or barrier. Anodic inhibitors are used to repair

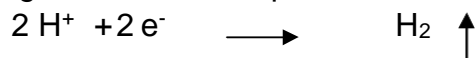
- a) the crack of the oxide film over the metal surface
- b) the pitting corrosion
- c) the porous oxide film formed on the metal surface.

Examples: Chromate, phosphate, tungstate, nitrate, molybdate etc.

Cathodic Inhibitors:

Depending on the nature of the cathodic reaction in an electrochemical corrosion, cathodic inhibitors are classified into

- a) **In an acidic solution:** the main cathodic reaction is the liberation of hydrogen gas, the corrosion can be controlled by slowing down the diffusion of H⁺ ions through the cathode. Eg., Amines, Mercaptans, Thiourea etc.



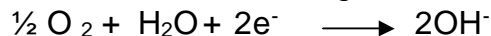
- b) **In a neutral solution:** in a neutral solution, the cathodic reaction is the adsorption of oxygen or formation of hydroxyl ions.

The corrosion is therefore controlled either by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathodic area.

The dissolved oxygen can be eliminated by adding reducing agents like Na₂SO₃.

The diffusion of oxygen can be controlled by adding inhibitors like Mg, Zn or Ni salts.

Eg., Na₂SO₃, N₂H₄, Salts of Mg, Zn or Ni.



Vapour phase inhibitors:

These are organic inhibitors which are readily vapourised and form a protective layer on the metal surface.

These are conveniently used to prevent corrosion in closed spaces, storage containers, packing materials, sophisticated equipments etc.

Examples are Dicyclohexylammonium nitrate, dicyclohexyl ammonium chromate, benzotriazole, phenylthiourea etc.

ANODIC PROTECTION

This is an electrochemical method of corrosion control in which an external potential control system, called potentiostat, is used to produce and maintain a thin non corroding, passive film on a metal or an alloy. The use of potentiostat is to shift corrosion potential into passive potential so that the corrosion of the metal is stopped.

The potential of the object (say acid storage tank) to be protected is controlled by potential controller (potentiostat) so that under certain potential range, the object becomes passive and prevents further corrosion. This potential range depends upon the relationship between the metal and the environment.

Applications:

1. Used in acid coolers in dilute sulphuric acid plants
2. used in storage tanks for sulphuric acid
3. used in chromium in contact with hydrofluoric acid

Limitations:

1. This method cannot be applied in the case of corrosive medium containing aggressive chloride.
2. This cannot be applied if protection breaks down at any point, it is difficult to reestablish.

PROTECTIVE COATINGS

Introduction:

In order to protect metals from corrosion, it is necessary to cover the surface by means of protective coatings. These coatings act as a physical barrier between the coated metal surface and the environment. They afford decorative appeal and impart special properties like hardness, oxidation resistance and thermal insulation.

Classification:

Protective coatings can be broadly classified into two types. They are

1. **Inorganic coatings**
- 2) **Organic coatings**

Inorganic coatings are further classified into two types. They are

i) Metallic coating :

1. Hot dipping- Galvanising, Tinning
2. Metal cladding
3. Cementation-Sherardising, Chromising, Calorising
4. Electroplating.

ii) Non-metallic coating:

1. Surface coating or chemical conversion coating – Chromate coating, Phosphate coating and Oxide coating.
2. Anodising
3. Enamel coating or Vitreous or Porcelain coating .

Organic coatings consists of

Paints, Varnishes, Lacquers and Enamels.

PAINTS

Paint is a viscous, opaque (not clear), mechanical dispersion mixture of one or more pigments (dye) in a vehicle (drying oil).

Requisites of a good paint:

A good paint should the following properties, it should

- 1) have a high hiding power
- 2) form a good and uniform film on the metal surface
- 3) the film should not crack on drying
- 4) give a glossy film
- 5) the film produced should be washable
- 6) give a stable and decent colour on the metal surface
- 7) have good resistance to the atmospheric conditions
- 8) be fluid enough to spread easily over the surface
- 9) possess high adhesion capacity to the material over which it is intended to be used
- 10) dry quickly or in a reasonable duration.
- 11) the colour of the paint should not fade.

Constituents of paint:

- a) Pigment
- b) Vehicle or medium or drying oil
- c) Thinner
- d) Driers
- e) Fillers or Extenders
- f) Plasticizers
- g) Antiskinning agents

a) Pigment:

It is a solid substance which imparts colour to the paint. It is an essential constituent of a paint. Its functions are to

- i) Give opacity (cloudiness) and colour to the film
- ii) Provide strength to the paint

- iii) Provide an aesthetical appeal
- iv) Give protection to the paint film by reflecting UV light.
- v) Increase weather resistance of the film
- vi) Provide resistance to paint film against abrasion.

The most commonly used pigments in paints and the compounds required as follows:

White pigments	-	White lead, ZnO, BaSO ₄ , TiO ₂ , ZrO ₂
Blue pigments	-	Prussian blue, ultramarine blue
Black pigments	-	Graphite, carbon black, lamp black
Red pigments	-	Red lead, Fe ₃ O ₄ , carmine
Green pigments	-	Chromium oxide, chrome green
Brown pigments	-	Burnt umber, ochre
Yellow pigments	-	Chrome yellow, lead chromate

b) Vehicle or drying oil or medium:

Vehicle is a liquid substance and film forming material . It holds all the ingredients of a paint in liquid suspension. Eg., linseed oil, tung oil.

Functions:

- i) To hold the pigment on the metal surface
- ii) to form the protective film by evaporation or by other means.
- iii) to impart water repellency, durability and toughness to the film
- iv) to improve the adhesion of the film

c) Thinners

Thinners are volatile substances which evaporate easily after application of the paint. They are added to the paints for reducing the viscosity of the paints so that they can be easily applied to the metal surface. Eg., Dipentene, turpentine, toluol, xylol.

Functions:

- i) To reduce the viscosity of the paint
- ii) To dissolve vehicle and the additives in the vehicle
- iii) To suspend the pigments
- iv) To increase the penetration power of the vehicle
- v) To increase the elasticity of the paint film
- vi) To help the drying of the paint film.

d) Driers:

These are the substances used to accelerate the process of drying. They are oxygen carrier catalysts. Eg., Naphthenates, linoleates, borates, resonates and tungstates of heavy metals (Pb, Zn, Co, Mn).

Functions:

- i) To accelerate the drying of the oil film through oxidation, polymerization and condensation

ii) To improve the drying quality of the oil film.

e) Extenders or Fillers:

These are the inert materials which improve the properties of the paint. Eg., Gypsum, chalk, silica, talc, clay, CaCO_3 , CaSO_4 .

Functions:

- i) To fill the voids (empty space or any curved area) in the film
- ii) To act as a carrier for the pigment color.
- iii) To reduce the cost of the paint
- iv) To increase the durability of the paint
- v) To reduce the cracking of dry paint
- vi) To increase random arrangement of pigment particles.

f) Plasticisers:

These are added to the paint to provide elasticity to the film and to minimize its crack. Eg., Triphenyl phosphate, dibutyl tartarate, tributyl phthalate, tricresyl phosphate, diamyl phthalate.

g) Antiskinning agents:

These are sometimes added to some paints to prevent gel ling and skinning of the finished product. Eg., Polyhydroxy phenols.

METALLIC COATINGS:

Corrosion of metals can be prevented or controlled by using methods like galvanization, tinning, metal cladding, electroplating, cementation, anodizing, phosphate coating, enamelling, electroless plating. Some of the methods are

1) Hot dipping:

It is used for producing a coating of low -melting metals such as Zn (m.p.=419 deg C), Sn (m.p.=232 deg C), Pb, Al etc., on iron, steel and copper which have relatively higher melting points. The process in immersing the base metal in a bath of the molten coating -metal, covered by a molten flux layer (usually zinc chloride).

2) Galvanizing:

It is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. The process is iron or steel article is first cleaned with dil. Sulphuric acid and washed with distilled water and dried. The dried metal is dipped in bath of molten zinc, now the thin layer of zinc is coated on the iron or steel article.

3) Metal cladding:

It is the process by which a dense, homogeneous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides. Corrosion resistant metals like nickel, copper,

lead, silver, platinum and alloys like SS, nickel alloys, copper alloys, lead alloys can be used as cladding materials.

4) Tinning:

It is a method of coating tin over the iron or steel articles. The process is first treating steel sheet in dilute sulphuric acid and it is passed through a flux ($ZnCl_2$), next steel passes through a tank of molten tin and finally through a series of rollers from underneath (bottom of) the surface of a layer of palm oil.

ELECTROPLATING OR ELECTRODEPOSITION

Electroplating is a coating technique. It is the most important and most frequently applied industrial method of producing metallic coating.

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

The base metal to be plated is made cathode whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity (like graphite).

Objectives:

Electroplating is carried out for

- 1) Decoration or better appearance
- 2) Increasing the resistance to corrosion of the coated metal.
- 3) Improving the hardness of the metal
- 4) Increasing the resistance to chemical attack
- 5) Electro refining.

Procedure:

The article is to be plated first treated with organic solvent like carbon tetrachloride, acetone, tetrachloro ethylene to remove oils, greases etc. Then it is made free from surface scale, oxides, etc. by treating with dil. HCl or H_2SO_4 (acid pickling). The cleaned article is then made as the cathode of the electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity. The electrolyte is a solution of soluble salt of the coating metal.

When direct current is passed, coating metal ions migrate to the cathode and get deposited there. Thus, a thin layer of coating metal is obtained on the article made as the cathode.

In order to get strong, adherent and smooth deposit, certain types of additives (glue, gelatin, boric acid) are added to the electrolytic bath.

In order to improve the brightness of the deposit, brightening agents are added in the electrolytic bath.

The favourable conditions for a good electrodeposit are

i) Optimum temperature ii) Optimum current density iii) Low metal ion concentrations.

Gold Electroplating:

Anode: Gold
Cathode: Metal article
Electrolyte: Gold + KCN
Temperature: 60 deg C.
Current density (mA cm⁻²): 1 -10

Use:

- i) This is used for electrical and electronic applications.
- ii) It is used for high quality decorations and high oxidation resistant coatings
- iii) Usually for ornamental jewellery, a very thin gold coating (about 1×10^{-4} cm) is given.

ELECTROLESS PLATING

Principle

Electroless plating is a newer technique of depositing a noble metal from its salt solution on a catalytically active surface of the metal to be protected by using a suitable reducing agent without using electrical energy.

The reducing agent reduces the metal ions into metal which gets plated over the catalytically activated surface giving a uniform and thin coating.



ELECTROLESS NICKEL PLATING:

Pretreatment and activation of the surface:

The surface to be plated is first degreased by using organic solvents or alkali, followed by acid treatment.

- i) The surface of the stainless steel is activated by dipping in hot solution of 50 % dilute sulphuric acid.
- ii) The surface of magnesium alloy is activated by thin coating of zinc or copper over it.
- iii) Metals (Al, Cu, Fe) and alloys like brass can be directly nickel plated without activation.
- iv) Non metallic articles like plastics, glass are activated by dipping them in the solution containing $\text{SnCl}_2 + \text{HCl}$, followed by dipping in palladium chloride solution. On drying, a thin layer of palladium is formed on the surface.

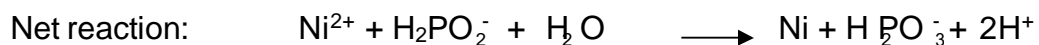
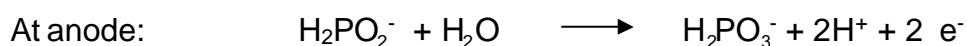
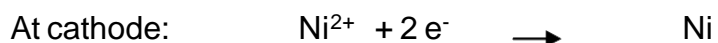
Preparation of plating bath:

The details of preparation of plating bath are:

Sl. No.	Nature of the compound	Name of the compound	Quantity (g/L)
1/	Coating solution	Nickel chloride (NiCl ₂)	20
2/	Reducing agent	Sodium hypophosphite (NaH ₂ PO ₂)	20
3/	Complexing agent	Sodium succinate	15
4/	Buffer	Sodium acetate	10
5/	Optimum pH	4.5	--
6/	Optimum temperature	93 deg C	--

Procedure:

The pretreated object is immersed in the plating bath for the required time. The following reactions occur and nickel gets coated over the object.



Applications:

- 1) It is used extensively in electronic appliances.
- 2) It is used in domestic as well as automotive fields (eg., jewellery, tops of perfume bottles).
- 3) Its polymers are used in decorative and functional works.
- 4) Its plastic cabinets are used in digital as well as electronic instruments.

