

Unit 2: CORROSION AND CORROSION CONTROL

CORROSION

Introduction:

- All metals and alloys are susceptible to corrosion.
- Au shows excellent resistance under atm condition, but gets corroded when exposed to Hg at ambient temp.
- On the other hand iron readily gets rusted in the atm but it does not corrode in Hg.

Definition:

- Corrosion is the disintegration of metal through an unintentional chemical or electrochemical action, starting at its surface.
- Rusting of iron($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)
- Cu sheeting on the roof of building develops green patina: $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- Ag article tarnishes and finally goes black in atm (Ag_2S)
- Tin plates in the can containing acid fruits (H_2 gas evolution).

Cause of Corrosion:

- Isolated pure metals can be regarded in excited state than their compound which are thermodynamically stable.
- Metals have natural tendency to revert back to their natural T.D stable combined state by forming compounds.
- When metals are put into use, they are exposed to environment, the exposed metal surfaces begin to decay by forming stable compounds(corrosion product).
- **Corrosion is a Reverse Extraction of metals**
- The magnitude of Gibbs free energy change predicts the tendency of corrosion reaction to occur. If ΔG is negative the corrosion is spontaneous and if it is positive, corrosion is not feasible.

Consequences of Corrosion: The process of corrosion is slow and occurs at the surface, but the losses incurred are enormous waste/destruction of machines, equipment.

- Plant shut down due to failure
- Replacement of corroded equipment
- Maintenance cost
- Loss of efficiency
- Contamination or loss of product(from the corroded container)
- Safety(fire due to release of toxic product or collapse of construction)
- Health(pollution)
- Necessity for over design to allow for corrosion
- **Approximate estimate of loss due to corrosion is 2 to 2.5 billion dollars per annum all-over the world**

TYPES OF CORROSION

Based on environment corrosion is classified into Two types.

1. Dry or Chemical Corrosion
2. Wet or Electrochemical Corrosion

I. DRY or CHEMICAL CORROSION

Definition: Direct chemical action of environment/atm gases such as O_2 , halogen, H_2S , SO_2 , N_2 or anhydrous inorg. liquid with metal surfaces of immediate proximity.

Types of chemical Corrosion:

a. **Oxidation Corrosion:**

- Brought by direct action of O_2 at low or high temp on metals, in absence of moisture.
- At ordinary temp. metals are very slightly attacked by O_2 .
- Even at low temp. alkali metals and alkaline-earth metals are rapidly oxidized.
- At high temp almost all metals (except Ag, Au, Pt) are oxidized.

Mechanism:

- Oxidation occurs first at the surface of the metal resulting in the formation of metal ions (M^{n+}).
- Oxygen changes to its ionic form (O^{2-}) by accepting the e-s donated by the metal.
- Metal surface is converted into its metal oxide by combination of metal ions and oxygen in the ionic form.
- For reaction (corrosion) to continue, either the metal ion diffuses outward through the metal-oxide layer to the surface or O_2 diffuses inwards through the layer to the underlying metal.
- Because of small size and high mobility of metal ion, outward diffusion of metal is much more rapid.
- Hence the nature of metal-oxide layer formed at the surface plays an important role in oxidation of corrosion process. The oxide layer or film decides the further reaction.

Nature of the metal-oxide layer or film

i) **Stable oxide Layer**

- Has fine-grained structure and gets tightly adsorbed to the metal surface.
- Impervious in nature and stops further O_2 attacks through diffusion.
- ***Behaves as protective coating and no further corrosion can develop***
- Eg. Oxides of Al, Sn, Pb, Cu etc

ii) **Unstable Oxide layer**

- Produced on the surface of the noble metals.
- Decomposes back into metal and O_2 .

Metal oxide \Rightarrow metal + O_2

- ***Oxidation corrosion is not possible***

- Eg. Ag, Au, Pt.

iii) **Volatile Oxide layer**

- Oxide layer volatilizes as soon as it is formed thereby leaving the underlying metal surface exposed for further attack.

- ***Causes rapid, continuous and excessive corrosion.***

- Eg. MoO_3 .

iv) **Porous Oxide Layer**

- Layer has pores or cracks in the layer.
- The atm O_2 has access to the underlying surface of the metal through the pores or cracks of the layer.
- ***Corrosion continues unobstructed till the entire metal is completely converted into its oxide.***
- eg. Alkali and alkaline earth metals.

PILLING – BEDWORTH RULE

• **Definition:** An oxide layer is protective or non-porous, if the volume of oxide is at-least as the volume of the metal from which it is formed.

On the other hand if the volume of oxide is less than the volume of the metal, the oxide layer is porous and non-protective, because it cannot prevent the access of O₂ to the fresh metal surface below. The ratio of the volume of the metal oxide to that of the metal is known as “specific volume ratio”.

- Greater the specific volume ratio, lesser is the oxidation corrosion rate.
- Specific volume ratio of Ni: 1.6, Cr: 2.0, W; 3.6. Corrosion of W is least even at elevated temp.
- Alkali and alkaline earth metals form oxides of volume less than the volume of these metals. So the oxide layers face stress and strains thereby developing cracks and pores in the structure.
- Metals like Al, forms oxide, whose volume is greater than the volume of the metal. Consequently an extremely tightly-adherent, non-porous layer is formed thereby the rate of oxidation rapidly decreases to zero.

b) Corrosion by other gases:

- Corrosion by gases like SO₂, CO₂, Cl₂, H₂S, F₂ etc.
- The extent of corrosion depends mainly on the chemical affinity between the metal and the gas involved.
- The degree of attack depends on the formation of protective or non-protective film on the metal surface.
- AgCl film, resulting from the attack of Cl₂ on Ag is non-porous and protective and so the intensity of the further attack decreases.
- If dry Cl₂ attacks tin (Sn), forms volatile SnCl₄. Consequently the whole metal is gradually destroyed.
- In petroleum industry, H₂S attacks steel at high temp. forming FeS which is porous and interferes with normal operations.
- **Hydrogen Embrittlement:** When metal contacts H₂S causes evolution of atomic hydrogen at ordinary temp. This atomic hydrogen diffuses readily into the metal and collects in the voids, where it combines to form molecular H₂. Collection of these gases in the voids develops very high pressure and causes cracks and blisters on metal. This process is called hydrogen embrittlement.



- **Decarburisation:** At high temp. the atomic hydrogen is formed by thermal dissociation of molecular H₂. When steel is exposed to this environment, the atomic hydrogen combines with carbon of the steel to produce methane gas. The process of decrease of carbon content of the steel is termed as decarburisation.



c) Liquid metal corrosion:

- Due to chemical action of flowing liquid metal on solid metal or alloy at high temp.
- It leads to either dissolution of solid metals by liquid metal or internal penetration of liquid metal into the solid metal thereby weakening of solid metal.
- Commonly occurs in devices used for nuclear power

II. WET or ELECTROCHEMICAL CORROSION:

- Occurs when a conducting liquid is in contact with metal or two dissimilar metals(or alloys) and multiphase alloy are either immersed or dipped partially in a solution
- Corrosion occurs due to existence of separate anodic and cathodic area or parts(electrochemical cell) between which current flows through the conducting solution.

- In two dissimilar metals (**galvanic corrosion**), the metal higher in electrochemical series acts as a cathode while other acts as an anode. In same metal electrochemical cell forms due to **localised stress** or due to **exposure to an solution of varying concentration or varying aeration**.
- *The mechanism of electrochemical corrosion is similar to that of electrochemical or voltaic ((galvanic) cell.*
- In anodic part of the metal oxidation takes place with the liberation of electron. The metal is destroyed either by dissolving or assuming combined state such as oxide. Hence corrosion occurs at the anodic area.
- In the cathodic part reduction takes place with the absorption of liberated electrons. The dissolved constituents in the conducting medium accepts the electrons to form some ions like OH⁻, O₂⁻.
- The metallic ions (at the anodic part) and non-metallic ions formed at the cathodic part diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and cathode.
- The rate of electrochemical reaction depends on the following factors
 - a) If the corrosion product goes into the solution without any difficulty, the corrosion rate continues the same.
 - b) If the corrosion product is an insoluble compound covering the metal surface, the corrosion rate will be considerably reduced.

Mechanism

At Anode:

- oxidation of metal takes place with the liberation of electron. The metal is destroyed either by dissolving or forming compounds (such as oxide, chloride etc)
- Hence corrosion occurs at the anodic area.

At cathode:

- Reduction takes place with the absorption of liberated electrons.
- The dissolved constituents in the conducting medium accepts the electrons to
- form some ions like OH⁻, O₂⁻ or cations like H⁺, accepts the electron

Two types of reaction

- 1) Evolution of hydrogen.
- 2) Absorption of oxygen.

1) Evolution of Hydrogen –Type

• Occurs in the acidic environment

• Reaction:



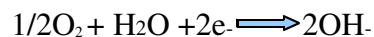
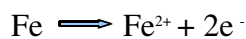
- Displacement of hydrogen ions from the acidic solution by the metal ions.
- All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.
- The anodic area is very large whereas the cathode area is small.

2) Absorption of Oxygen or Formation of Hydroxide

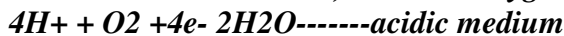
• Occurs when the base metals are in contact with neutral solution like water, NaCl or moisture with dissolved oxygen.

- The best example is rusting of iron.
- If rust, iron oxide coats the surface as thin film. If the film develops some cracks, the exposed metal areas act as anodes while the covered part form large cathodes.
- Anodic parts are very small compared to the cathode parts and leads to localized corrosion.

• Reaction

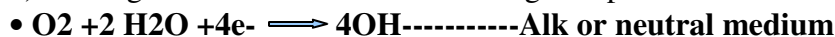


- If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide (yellow rust).
- If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite.
- The corrosion product, rust is deposited at or near the cathode part, because of rapid diffusion of small Fe^{2+} ion than the larger OH^- ions
- *Even in acidic medium, dissolved oxygen accepts electrons, i.e., absorption of oxygen takes place.*



The increase in oxygen content enhances the corrosion by either

1) Forcing the cathodic reaction to the right to produce more OH^- ions



2) Removing more electrons and thereby accelerates the corrosion at the anode.



Salient Features of Electrochemical corrosion

- Formation of anodic and cathodic areas or parts in contact with each other
- Presence of conducting medium
- Corrosion occur at anodic areas only
- Formation of corrosion product between anode and cathode
- Some times more than one reduction reactions i.e., both evolution of hydrogen and reduction of oxygen take place. If two types of reduction reaction take place, the corrosion is severe
- Ex: When zinc is dipped in aerated acid

DIFFERENCES BETWEEN CHEMICAL AND ELECTROCHEMICAL CORROSION

Chemical Corrosion

- 1) It occurs only in dry condition
- 2) It is due to the direct chemical attack
- 3) Even a homogeneous metal surface
- 4) Corrosion products accumulate at the place where corrosion occurs.
- 5) Self-controlled
- 6) Follow absorption mechanism
eg. Formation of mild scale on iron
When exposed to atm.

Electrochemical Corrosion

- Occurs in presence of moisture or electrolyte
- Due to the set up of a large number of metal by the environment cathodic and anodic areas.
- Heterogeneous surface or bimetallic contact gets corroded.
- Corrosion occurs at the anode while corrosion product forms elsewhere.
- Continuous process
- Electrochemical Reaction
- Rusting of iron in moist atm.

TYPES OF ELECTROCHEMICAL CORROSION

The principle of electrochemical corrosion is involved in the following types of corrosion

1. Galvanic Corrosion
2. Concentration Cell Corrosion (Differential Aeration Corrosion)
3. Stress Cell Corrosion

Concentration Cell Corrosion (refer Text Book)

1. Pitting Corrosion
2. Crevice Corrosion
3. Caustic Embrittlement

4. Microbial corrosion
5. Waterline corrosion
6. Pipeline corrosion
7. Wire fence corrosion

GALVANIC CORROSION

• When two dissimilar metals are in contact (joined by riveting or welding) and jointly exposed to an electrolyte, the metal higher in the electrochemical series undergoes corrosion.

• The metal lower in the electrochemical series becomes cathode and it is protected from the attack.

• **Mechanism:**

At Anode: Corrosion occurs.

At Cathode: In acidic solution hydrogen evolution is the cathodic reaction while in neutral or slightly alkaline solution oxygen absorption takes place.

Eg. Steel screws in brass marine hardware
Steel pipe connected to Cu plumbing
Pb-As solder around Cu wire.

Galvanic corrosion can be avoided by

- Fixing an insulation material between the two metals.
- Making the cathode metal smaller and anode metal
- coupling metals close in the emf series or galvanic series

GALVANIC SERIES

Limitation of emf series:

1. It could not explain some exceptions to this generalization.

• According to emf series a metal higher in the series is more anodic and undergoes corrosion faster than the metal below it. But

• Zn-Al couple: **Zn(-0.76)** is below **Al(-1.66)** in the emf series but it behaves like anode and is corroded while Al acts cathode.

• Ti is above Ag in the series but it is less reactive than Ag.

• Metals like Ti and Al develop strong, adherent oxide layer on their surfaces, thereby making their **effective electrode potential more positive** (or less negative).

2. Emf series does not account for the corrosion of all metals and alloys.

Galvanic Series: Refer book

• A more practical series have been prepared by studying the corrosion of metals and alloys in a given environment like sea-water.

• It gives real and useful information about the corrosion of metals and alloys.

EMF series	Galvanic series
<ul style="list-style-type: none">• Electrode potential is measured by dipping pure metal into their solutions of their own ions• The position of metal in emf series is fixed• No information regarding the position of alloys• Series comprises of metal and non metals• It predicts relative displacement tendencies	<p>Alloys and metals into unpolluted sea water after removing the surface oxide film.</p> <p>The position may shift in different environment</p> <p>The position of alloy is different from that of pure alloy. Alloys are included</p> <p>Comprises metals and alloys</p> <p>It predicts the relative corrosion tendencies</p>

CONCENTRATION CELL CORROSION

- Due to the electrochemical attack of metal exposed to an electrolyte of a varying concentration or varying aeration.
- Concentration cell forms as a the result of local difference in metal-ion concentration caused by local temp. difference or inadequate agitation or slow diffusion of metal ions produced by corrosion.

DIFFERENTIAL AERATION CORROSION

- Common type of concentration cell corrosion.
- Poor-oxygenated part acts as anode and gets corroded.
- More O₂ concentrated part becomes cathodic.
- Differential current flows between the anode and cathode.
- Eg.i) Corrosion of metals partially immersed in solution just below the water line. ii) Corrosion of iron under drops of water.

General facts about differential aeration corrosion

1. Corrosion may be accelerated in apparently inaccessible place.
2. Corrosion may be accelerated under accumulation of dirt, sand, scale or other.
3. Metals exposed to aqueous media corrode under blocks of wood or piles of glass, which screen that portion of the metal from oxygen access.

Mechanism

At anode: Corrosion occurs

At Cathode:

Acidic Medium: Either hydrogen evolution or oxygen reduction

Basic Medium : Hydroxide formation

Different Types of Differential Aeration Corrosion

- 1) **Waterline Corrosion:** Maximum corrosion takes place along the line just beneath the level of water meniscus.
- 2) **Pitting corrosion:** Metal area covered by a drop of water and sand, dust, scale etc.
- 3) **Crevice Corrosion:** If a crevice between different metallic objects or between metal and non-metallic material is in contact with liquid, the crevice becomes the anodic region and suffers corrosion.
- 4) **Pipe line corrosion:** Differential aeration corrosion may also occur at the different parts of pipeline. Buried pipelines or cables passing from one type of soil to another, from clay (less aerated) to sandy (more aerated) sand.
- 5) **Corrosion on wire fence:** The areas where the wire-cross are less aerated than the rest of the fence and hence corrosion occurs at wire crossing which are anodic.
- 6) **Caustic Embrittlement:** Because of conc gradient of NaOH, conc cell corrosion takes place in the boiler
- 7) **Microbial corrosion (also called microbiologically-influenced corrosion or MIC)**
 - Most MIC takes the form of pits that form underneath colonies of living organic matter and mineral and bio deposits.
 - These colonies restrict the flow of O₂ to the surface which results in differential aeration corrosion.

FACTORS INFLUENCING CORROSION

The rate and extent of corrosion depends on

1. Nature of metal(substrate) and
2. Nature of corroding environment

1. NATURE OF METALS (SUBSTRATE)

ii) Position in the galvanic series:

- Extent of corrosion depends on the position of metal in emf or galvanic series
- Zn ($E^0 = -0.76$) corrodes faster than Ni ($E^0 = -0.23$)
- Metals above H₂ in emf series get corroded vigorously
- The more active metal (or higher up in the series) suffers corrosion when two metals or alloys are in electrical contact. (**galvanic corrosion**).
- The greater is the difference in their position, the faster is the corrosion of anodic metal/alloy.
- The pot. diff. between the anode and cathode is the driving force of an electrochemical reactions
- The greater is the difference in their position, the faster is the corrosion of anodic metal/alloy

iii) Over Voltage(Back emf):

- Evolution of hydrogen is one of the cathodic reactions in corrosion.
- When electrolysis carried out, the products accumulate around the electrode, change the concentration around the electrodes and hence the electrode gets polarized.
- Polarization is a process wherein, there is a variation of electrode pot. due to conc gradient at the electrode due to slow diffusion of ions which develops opposing emf or back emf.
- Because of back emf potential, higher than the theoretical potential is needed to carry out the anodic reaction (corrosion) and cathodic reaction (H₂ evolution)
- The difference of potential that exist between a reversible H₂ electrode and an electrode in the same solution at which H₂ is being formed from H⁺ ions-

Hydrogen over voltage.

- Rate of corrosion can be reduced by increasing the hydrogen over voltage.
- On the other hand reduction of hydrogen over voltage by addition of foreign ion accelerates the corrosion of metal/alloy.
- Eg. The addition of few drops of CuSO₄ to acidic solution where Zn is placed.

iv) Relative areas of anodic and cathodic parts

- Corrosion of the anodic part is directly proportional to the ratio of areas of cathodic and anodic part.
- The corrosion is more rapid, severe and highly localized if the anodic area is small since the demand for electrons by large cathodic area can be met by smaller anodic area by undergoing "corrosion more briskly".
- Eg. Small steel pipe fitted with a large Cu tank.

v) Purity of the metal

- Impurities in the metal cause heterogeneity and form minute tiny electrochemical cells and anodic parts get corroded.
- Even a trace amount of impurity causes galvanic corrosion
- Higher the % of impurity faster the rate of corrosion
- Eg. Al metal containing impurity

%purity of Al	99.99	99.97	99.20
Relative rate of corrosion	1	1000	30,000

vi) Physical state of metals

- The smaller the grain-size of metal or alloy, the greater will be its solubility and greater will be its corrosion.

- Even in a pure metal, areas under stress tend to be anodic and leading to corrosion.

vii) Nature of surface film

- In aerated atm, practically all metals get covered with a thin surface film of metaloxide.
- The ratio of the volume of the metal oxide to that of the metal is known as “specific volume ratio”.
- Greater the specific volume ratio, lesser is the oxidation corrosion rate.
- Specific volume ratio of Ni: 1.6, Cr: 2.0, W; 3.6. Corrosion of W is least even at elevated temp.

viii) Passive character of the metal

- Metals like Ti, Al, Cr, Mg, Ni and Co are passive due to the formation of highly protective, thin film of oxide on the metal or alloy surface.
- They exhibit much higher resistance than expected from their position in galvanic series.
- Oxide film on Cr has self-healing nature, if broken it repair itself on re-exposure to oxidizing condition. Corrosion resistance of stainless steel is due to passive and self-healing character of Cr present in it.

ix) Solubility of corrosion product

- If the corrosion product is soluble in the corrosive medium, corrosion proceeds at a faster rate.
- If the corrosion product is insoluble or forms another insoluble product by interaction with the medium, the corrosion product functions as a physical barrier, thus by suppressing further corrosion.
- Eg. PbSO_4 formation in case of Pb in H_2SO_4 .

x) Volatility of corrosion product

- If the corrosion product volatilizes as soon as it is formed, leaving the underlying metal exposed to further attack.
- Eg. MoO_3

2. NATURE OF CORRODING ENVIRONMENT

i) Temperature of the corroding medium

- Rate of corrosion reaction increases as diffusion rate of ions are increased.

ii) Humidity of the air

- **Critical humidity:** The relative humidity of atm above which the corrosion rate of metal increases sharply. It is decided by the nature of the metal as well as corrosion product.
- If atm air contains CO_2 , O_2 etc the moisture furnish electrolyte and form electrochemical cells.
- If oxide film on the metal is hygroscopic it absorbs moisture and makes electrochemical cell.
- Humidity or rain water supply necessary moisture for electrochemical attack. Besides they may also wash away part of oxide film on the surface which leads to concentration cell corrosion unless the oxide film is exceptionally adherent.(Cr and Al)

iii) Impurities present in the atm

- Atm vicinity of industrial areas contains corrosive gases like CO_2 , H_2S , SO_2 , fumes of HCl , H_2SO_4 etc.
- These gases increase the acidity of the liquid, electrical conductivity and corrosion current.
- In marine atm the presence of Na and other chlorides increase the conductivity of the sea water and thereby corrosion is speeded up.

iv) Presence of suspended particle

- If the suspended particles are chemically active in nature, they may absorb moisture and act as strong electrolytes.[ex. NaCl , $(\text{NH}_4)_2\text{SO}_4$].
- Even the chemically inactive suspended particles absorb the impurities present in the air and become active and slowly enhance the corrosion rate.

v) Influence of pH

- Determined by the nature of its oxide.
- If the oxide is acidic, soluble in acidic media and gets corroded vice versa.
- Amphoteric metals like Al, Zn, Pb dissolve in acidic and alkaline medium and form complex ion but they have greatest stability at some intermediate pH range, like 6-7 and above 11.5
- If metal oxide is insoluble at any pH, its corrosion rate is independent of pH
- Generally acidic media are more corrosive than alkaline and neutral media.
- Metal is readily attacked by even weak acid in presence of oxygen.

vi) Nature of ions present

- Anions like silicate form insoluble reaction product (silica gel) which inhibit further corrosion.
- Chloride ions destroy the passive surface films thereby expose metal/alloy surface for fresh corrosion.

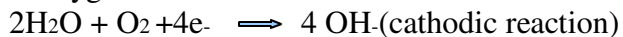
vii) Conductivity of corrosive medium

- Conductance of the medium is very important for the underground and submerged structure.
- Conductivity of dry sandy soil is lower than those of clay or mineralized soil. Stray current (Power from leakage) will cause more severe damage to the metallic structure under clay and mineralized soil.

viii) Formation of oxygen concentration cell

- Increasing supply of O₂/air to the moist metal surface promote the corrosion by oxygen concentration cell formation.

- Less O₂ concentrated part, oxide coated part, or less exposed part becomes anodic
- More O₂ concentrated part becomes cathodic.
- Oxygen concentration cell forms and corrosion takes place at the cathode.



ix) Flow velocity:

- Flow velocity is an important environmental factor.
- ***Increasing the flow velocity of medium enhances the diffusion rate of ions thereby increases corrosion rate.***
- Its effect is especially pronounced in chemical processing, petroleum, marine, and power plants, which handle fluids of all kinds.
- Film thickness, and thus the resistance, of surface films, is reduced by high flow velocities
- At critical or breakaway velocity, surface film resistance almost vanishes, the products of corrosion and protective film are continuously swept away, and continuous corrosion occurs.
- This type of corrosion has been observed on brass condenser tubes through which a medium flows at a high velocity, and it is severe at places where the velocity changes rapidly, such as at bends and in valves.

X) Polarization (Back emf)

- The pot diff between the anode and cathode is the driving force of an electrochemical reaction like corrosion.
- When metal undergoes corrosion, corrosion takes place at the anode while H₂ evolution occurs at the cathode.
- The corrosion products formed as a result of corrosion gets accumulated around the electrode and change the concentration around the electrodes or polarize the electrode which develops opposing emf or back emf.
- Polarization is a process wherein, there is a variation of electrode pot. due to conc gradient at the electrode due to slow diffusion of ions.

- Because of back emf potential, higher than the theoretical potential is needed to carry out the anodic reaction (corrosion) and cathodic reaction (H₂ evolution)
- **The potential difference between the theoretical and actual value is called over voltage.**
- corrosion is quite slow because of over voltage
- *The corrosion can be reduced by adding certain additives (inhibitors) to the corroding environment by polarization*

CORROSION CONTROL

It is impractical to eliminate corrosion but corrosion can be controlled and minimized by several methods. The rate of corrosion can be controlled by either modifying the base metal/alloy or the environment.

- I. Control of corrosion by modifying metal:
 - a) Modifying the composition of metal/alloy
 - b) Proper designing.
 - c) Modifying the surface.
- II. Control of corrosion by modifying the environment
 - a) Removal of harmful constituents
 - b) Use of inhibitors
 - c) Modifying the energetic condition by electrochemical means.

I. CONTROL OF CORROSION BY MODIFYING THE BASE METAL

a) Modifying the composition of the metal:

- i) Pure metal:
 - Impurities cause heterogeneity and leads to electrochemical corrosion.
 - Corrosion resistance of pure metal depends on the nature of environment.
 - Al in the pure form gives coherent, impervious, protective film. But in alkaline medium, the oxide film is destroyed
 - In many cases it is not practical to produce pure metal because of high cost and inadequate mechanical properties like softness and low strength.
- ii) Alloying:
 - Alloy should be completely homogeneous.
 - Because of the self healing effect of Cr, it enhances the corrosive resistance of stainless steel.

b) Proper Designing:

1. Avoid the contact of dissimilar metals.
2. Choose high anode area.
3. Choose the metal which are close in the emf series.
4. Insulate the fitting of different metals.
5. Anodic metal should not be painted.
6. Prevent homogeneities.
7. Avoid sharp corners and crevices.
8. Avoid stress.
9. Equipment should be supported.

c) Modifying the surface by application of protective coatings.

- The coated surface isolates the underlying metal from the corroding environment.
- The coating applied must be chemically inert to the environment under particular condition of temp. and press.

- Important protective coatings are metallic coatings, Organic coatings and Chemical Conversion coatings.

Metallic Coatings: Two Types

Anodic Coatings:

- Produced from coating-metal which are anodic to the base metal.
- If any break or discontinuities occur in such anodic coatings, a galvanic cell is formed between the coating-metal and the exposed part of the metal.
- The coating metal (being anodic) is attacked leaving behind the underlying base metal unattacked.
- Eg. Galvanised steel.

Cathodic Coatings:

- Obtained by coating of noble metal than the base metal.
- They protect the base metal because they have higher resistance than the base metal.
- They provide effective protection to the base metal only when they are completely continuous and free from pores, breaks and discontinuities.
- If such coatings are punctured, much more corrosion damage can be done to the base metal.
- The exposed base metal acts as anode and intense localized attack occurs at the small exposure.
- Eg. Tin-coating on steel.

Organic coatings:

Inert organic-barriers (like paints, varnishes, lacquers and enamels) applied on metallic surfaces for both corrosion protection and decoration.

Chemical Conversion Coatings:

Inorganic surface-barriers produced by chemical or electrochemical reactions, brought about at the surface of the metal.

They are particularly used as an excellent base for organic coatings.

II. CORROSION CONTROL BY MODIFYING THE ENVIRONMENT

a) By Removal of harmful constituents:

Deaeration: removal of oxygen by mechanical methods.

Deactivation: Removal of oxygen by compound formation.

Dehumidification: removal of moisture in air.

Alkaline neutralisation: Neutralise the acidic environment.

b) Use of Inhibitors:

A substance which when added in small quantities to the aqueous environment effectively decreases the corrosion of metal.

i) Anodic Inhibitors:

They shift the corrosion reaction occurring at the anode by forming a sparingly soluble compound with the newly produced metal ion.

The compounds are adsorbed on the metal surface forming protective film or barrier thereby reducing the corrosion rate.

- Although this type of control is effective, it may be dangerous, since severe local attack can occur, if certain areas are left unprotected by the depletion of the inhibitor.

- Eg. Chromates, phosphates, tungstates or other ions of transition elements with a high oxygen content.

ii) Cathodic Inhibitors:

- In acidic solution: Corrosion may be reduced either by slowing down the diffusion of hydrated H^+ ions to the cathode, and/or by increasing the overvoltage of hydrogen evolution.
- The diffusion of H^+ ions is considerably decreased by organic inhibitors which are capable of being adsorbed at the metal surface.
- Antimony and arsenic oxides deposit adherent film of metallic arsenic or antimony at the cathodic areas, thereby increasing considerably the hydrogen overvoltage.
- In neutral solutions: Corrosion can be controlled by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathodic areas.
- Adding reducing agents like Na_2SO_3 or by deaeration the oxygen can be eliminated.
- The inhibitors like Zn, Ni salts react with hydroxyl ions at the cathode forming corresponding insoluble hydroxide which act as impermeable self-barriers.

Modifying the energetic condition by electrochemical means.

i) Cathodic Protection: The metallic structure is forced to behave like cathode thereby corrosion does not occur.

Sacrificial anodic protection method

- The metallic structure to be protected is connected by a wire to a more anodic metal like Zn, so that all corrosion is concentrated at this more active metal.
- The more active metal itself corroded slowly while the metallic structure is protected.
- The more active metal is called “sacrificial anode” and it is replaced by fresh one, when consumed completely.
- Buried pipelines, underground cables, marine structures, ship-hulls, water-tanks, piers, etc.

Impressed current cathodic protection:

- An impressed current is applied to in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.
- Impressed current is derived from DC source(battery) with an insoluble anode(graphite).
- Anode is in backfill(composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil.
- A sufficient d.c current is applied to insoluble anode, buried in the soil or immersed in the corroding medium and connected to the metallic structures to be protected.
- It is useful for large structures for lon-term operations.eg. buried water or oil pipes, water tanks.

METALLIC COATINGS

- They act as a continuous physical-barriers between coated-surface and its environment and protect the metal surface from corrosion.
- They give decoration
- They improve the physical and mechanical properties

METHODS OF APPLICATION OF METALLIC COATINGS

- Displacement or immersion plating
- Metal spraying or metallized coatings
- Cementation or diffusion coating

- Metal cladding
- Hot Dipping
- Electroplating
- Electroless Plating

Surface Preparation for protective coatings

Aim

- Metal surfaces are covered with rust, oxide scales, oil, grease, org. compounds etc-These substances lead to porous, discontinuous or non-adherent coatings
- To get uniform, smooth, cohesive and adherent coating these unwanted substances should be cleaned perfectly
- ***Non adherent coating leads to blistering, peeling, rough non-uniform coating which results in galvanic corrosion***

Adherent, uniform coating enhances

- *Corrosion, abrasion and thermal resistance,*
- *Optical and thermal reflectivity*
- *Quality of electrical and electronic components like capacitors, contacts, PCB*

Different methods of surface cleaning

I. Mechanical Methods

- *Using Impact tools and brushes*
- *Sand Blasting*

II. Chemical Cleaning

- *Solvent Cleaning*
- *Pickling and Etching: Acid and Alkali cleaning*
- *Flame Cleaning*

III. Electro Cleaning

- *Cathodic cleaning*
- *Anodic Cleaning*

I. Mechanical Cleaning

Using Impact tools and brushes

- Free the surface from a skin of damaged metal. E.g., loose fragments, scratches and strains produced by mechanical operation
- Removal of all rust scale, mild scale, loose paint, and loose rust
- The different methods are hammering, scrapers, wire-brushing, grinding, polishing, sand-blasting
- Instruments like hammers, knife scrapers, bristle brush, grinding and polishing wheel are used to remove strongly adherent scales.
- Power wire brushes, power impact tools, power grinders, power sanders or by a combination of these methods
- Grinding and polishing are widely used for pretreatment of metal surfaces which are to receive paints, lacquer and enamels
- It is followed by Solvent cleaning or steam or hot water treatment

Sand Blasting:

- Priming a surface for the application of paint or a sealant.
- Avoid trapping of dust, dirt, or bubbles in a previous layer of paint, or other imperfections under the new layer.

Process: By launching small bits of abrasive (sand) at the surface at a high speed under pressure of 25 to 100 atm, all imperfections are knocked loose and can then be easily washed off

Advantages:

- Used for cleaning the hulls of ships or large structures
- Used for removing oxide scales, particularly when a slightly roughened surface is desired
- Paint coatings on sand-blasted surface are more durable than those on other methods
- Improves and hardens the surface

Disadvantages

Require expensive equipment dangerous to the health of workers, because of the possibility of disease silicosis

II. Chemical Methods

Solvent Cleaning: Degreasing

- Used to remove oils, grease and org. compounds
- Org. solvents like naphtha, chlorinated hydrocarbon, toluene, xylene or acetone are applied in the first step.
- It is followed by cleaning with *steam and hot water containing wetting agents and alkalis* to provide wetness to the surface which is necessary for electroplating

Flame Cleaning

- Removal of all loose scale, rust and other detrimental foreign matter by passing high temperature, high velocity oxy-acetylene flames over the entire surface, followed by wire brushing.
- Removes oil, grease, dirt, soil, salts and other contaminants

Pickling and Etching

Alkali Cleaning

- This is the *most common type* of cleaning method employed.
- To remove old paints
- The cleaning compounds used are cheap and so the process is relatively *cost effective*.
- Agents are trisodium phosphate along with soaps and wetting agents like caustic soda
- After cleaning with the alkali solution, parts must be thoroughly rinsed with water and then immersed in slightly acidic solution of 0.1% Chromic acid or Na or K dichromate to remove last traces of alkalis
- Al is pickled in alk cleaning

Acid Pickling

- *More convenient method*
- Immersed inside the acid solution with some inhibitor at warm condition for long duration
- Acids like H₂SO₄, HCl, HF, H₃PO₄ are used under in dil condition
- All metals except Al, can be pickled in acid solution.
- Steel is cleaned by dipping in warm dil H₂SO₄ or cold HCl containing some inhibitor
- For Cu, brass and Ni, HNO₃ or mixture of dil.HNO₃ and dil H₂SO₄ is used

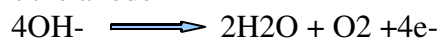
III. Electrocleaning

Making metallic articles as either cathodic or anodic in an electrochemical cell

The basic functions of electro cleaners are

- To remove soil that can not be removed other methods
- To remove adherent residues
- To remove oxidation products
- Alkali is a conducting medium

At the anode



At the cathode



Anodic Electro cleaning

- Making *metal anodic*
- Anodic electro cleaning is used for final cleaning.
- The metal surface is being dissolved as well as cleaned
- This depleting action removes metallic smuts and prevents the deposition of non-adherent metallic films and particles.
- At the interface of the anodic part's surface and the solution, oxygen is liberated. It creates a mechanical scrubbing action that loosens and lift the soil.
- For anodic cleaning, low voltage (3–12 volts) is normal. Current densities vary from 10–15 asf, depending on the metal being cleaned Cleaning times of 1/2 – 2 minutes generally. Higher current densities may be used when cleaning times is shorter
- Used in rare cases where the oxide scales cannot be removed by other methods

Cathodic Electro cleaning

- Making *metal cathodic*
- Hydrogen rather than oxygen is liberated at the surface of the work.
- Evolution of H₂ at cathode results in strong agitation and helps to dislodge the oily substances
- The volume of hydrogen liberated at the cathode is twice that of oxygen liberated at the anode, for a given current density
- Therefore, more gas scrubbing is achieved at the cathode than at the anode
- Evolution of H₂ at cathode results in strong agitation and helps to dislodge the oily substances
- The same equipment, voltages and current densities specified for anodic cleaning are generally satisfactory for cathodic cleaning
- Direct-current cleaning is generally used to clean these metals and to clean buffed nickel prior to chromium plating.
- Anodic cleaning would leave a passive nickel oxide film, which prevents the proper deposition of chromium.

Preparation of Non-metallic surfaces

- Synthetic plastics such as vinyl chloride, bakelite, cellulose derivative can be polished by methods comparable to those used in case of metals
- Leather, paper, cloth are cleaned to remove oils, grease, waxes and then rendered non-porous by coating with shellac or lacquer
- The conducting surface is produced by depositing continuous coating of Cu or Ag by chemical reduction or metal spraying or by sputtering at high voltage

METALLIC COATINGS

Functions of Metallic Coatings

- Improve the corrosion resistance of less-costing, easy corroding materials- Act as continuous physical-barriers between coated-surface and its environment and protect the metal surface from corrosion.
- Improve the appearance of metals/alloys
- Improve the physical and mechanical properties

Requisites of metallic coatings

- Chemically inert to the environment, under particular conditions of temp and pressure
- Prevents the penetration of environment to the base metal

METHODS OF APPLICATION OF METALLIC COATINGS

- 1) Displacement or immersion plating
- 2) Metal spraying or metallized coatings
- 3) Cementation or diffusion coating
- 4) Metal cladding
- 5) Hot Dipping
- 6) Electroplating
- 7) Electroless Plating

Electro deposition-Electroplating

- The process by which the coating metal is deposited on the base metal by passing a d.c through an electrolytic solution containing the soluble salt of the coating metal.
- The film (electro deposit) produced is quite uniform, with a little or few pinholes per unit area.
- Depositing a thin layer of superior metal(or alloy) over an inferior one by passing direct current

Objectives

Deposits on metals

- Improves resistance to corrosion
- Improve physical appearance and hardness
- Improve thermal insulating and electrical properties
- Decoration

On non metals

- To increase the strength
- To make the surface conductive
- To preserve and decorate the surface

Characteristics of electrodeposits

Thickness

- Thickness of the deposit should be minimized in order to get a strong adherent coating
- Multiple coatings is given in order to make sure that coating is completely free from pores and discontinuity
- Thin deposits are used for decorative purpose while thick deposits are used for corrosion protection
- Measured by Gauges, Coulometer and X-ray
- In the range of micrometer

Adherence

- Weak adherence leads to peeling off
- It can be measured by methods like bending, twisting, sudden heating or cooling

Hardness:

- It is very important if the purpose of electroplating is to improve corrosion resistance
- Measured in Brinells
- Ranges from 5 to 1,000 Brinells

Protective value

- Depends on thickness and porosity
- Nonporous and thicker coating has more protecting power

Decorative Value

- Coating should be free of stain and discoloration

- The liberation of H₂ along with deposit can cause blistering and pitting off the deposit and gives dull appearance.

Theory

- *Depositing a thin layer of superior metal (or alloy) over an inferior (base) one by passing a direct current (D.C) through an electrolyte solution containing metal ions to be deposited*

Cathode:

- The base metal to be plated is made as the cathode of the electrolytic cell

Anode

- The anode is either made up of coating metal(soluble anode) itself or an inert material(insoluble anode) of good electrical conductivity

Soluble anodes:

- The concentration of bath/solution remains unaltered, since the metal ions deposited from the bath are replenished continuously by the reaction of free anions with the anode metal.
- The anode is replaced once it is consumed

Insoluble anodes:

- The salt is added continuously in order to maintain the concentration of the electrolytic bath
- The process of electroplating goes on non-stop, since the anode is not consumed and its replacement is not required

Procedure:

1. The article to be electroplated is first treated with chemical cleaning with org. solvent and then by acid cleaning.
2. The cleaned article is made as a cathode of an electrolytic cell
3. The anode is either the soluble or insoluble type
4. The bath is prepared by dissolving the salts of base metal along with some additives
5. The anode and cathode are dipped in the electrolytic solution
6. When d.c current is passed, deposition takes place on the surface of the cathode
7. The required time ranges from a few sec to 30 min.
8. Thickness of deposit ranges from 0.01 to 100 μm

Factors Influencing electro deposition

1. Cleanliness of the article to be plated

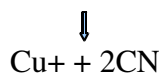
- A well cleaned properly pre-treated surface is essential for strong, adherent coating
- Maximum coating adhesion can be obtained only the metal surface is free from any dirt and corrosion product

2. Temperature of the bath

- Usually kept between 35-60 C , temp close to room temp
- Warm baths are also used
- Increases the solubility of electrolyte, increases the conc of metal ion and thereby reduces current density
- Decreases the crystal size of, thereby lowering the cost of electrical energy
- High temp is avoided as it accelerates H₂ evolution which leads the corrosion of equipment

3. Composition of the Electrolyte

- Low metal ion conc is preferred as they give rise to very adherent coating
- It is achieved by using complexing agent or using common ions
- Different stages of ionization of metal ions and so produces lesser amts of ions
- $\text{Na}[\text{Cu}(\text{CN})_2] \rightleftharpoons \text{Na}^+ + [\text{Cu}(\text{CN})_2]^-$



- Due to complex ion, produces lesser metal ions

4) Choice of Electrolyte

- Electrolyte should be
- A good conductor
- Highly soluble
- Not undergo hydrolysis, oxidation, reduction or other chemical changes
- Sufficient throwing power
- No single electrolyte satisfy all these requirement
- To improve conductivity non-participating electrolytes are added
- Ex. Addition of H_2SO_4 to CuSO_4 bath

5) Throwing Power

- Ability of electrolyte cell to give deposit of uniform thickness over the entire cathode area
- When cathode is in regular shape maximum cathode power is exhibited
- When it is in irregular shape, the throwing power can be improved by
- Agitating the solution to minimize the high local electrolyte conc
- Separate the distance between the electrodes by using auxiliary anodes

6) Current Density

- Current per unit area of the object being plated
- Expressed in Acm^{-2} , Am^{-2} , Aft^{-2}
- The c.d should be minimum optimum value
- If it is high, the deposits become loose and brittle
- If is very low the rate of electro deposition is quite low and it takes long time to finish the job

7) pH of the bath

- Must be properly maintained to get deposition effectively
- Optimum pH is obtained from experience
- pH is mainlined by using buffers
- pH lower than optimum value leads to H_2 evolution which results in burnt deposit
- Higher value leads to pptation of hydroxides at the electrode surface
- pH ranges from 4 (moderately acidic) to 8 (slightly alkaline)

8) Additives

- Nature of the deposit is remarkably influenced by additives
- Added to get strong, adherent and mirror- smooth coating
- Added in small quantities
- Brighteners, levelers, structure modifiers and wetting agents
- Ex. Gelatin, glue, boric acid

9) Agitation

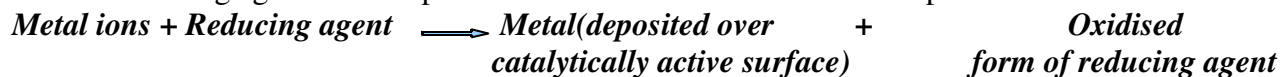
- Agitating the solution to minimize the high local electrolyte conc
- Should not be used great extent because it may lead to rough depn and increase the temp of the bath

Electroplating bath composition for Au: refer book

Electroless Plating (Chemical Plating)

- Deposition of noble metal ion (from its salt solution) on a catalytically active surface of a less noble metal by employing a suitable reducing agent without passing current
- The base substrate being plated must be catalytic in nature.

- Minute amount of the electroless metal itself catalyze the reaction, and the deposition is autocatalytic after original surface is are coated
- Reducing agent causes the reduction of metallic ion to metal which eventually gets plated over the catalytically activated surface giving highly uniform thin coating
- Reducing agents are simple electron donors and metal ions accept the electrons



- Driving force is autocatalytic redox reaction on pretreated catalytic surface
- Differs from immersion plating in that the deposition of metal is autocatalytic or continuous

Preparation of Active Surface to be plated

- Etching by acid pickling
- Electro plating a thin layer of the same metal followed by heat treatment
- Treated with stannous chloride followed by dipping in Pd. Chloride which yields thin layer of Pd-Plastics and printed circuit board

Composition of Plating bath

- Metal ion- soluble salt like chlorides, sulphates
- Reducing agent- formaldehyde, hypophosphite
- Complexing agent- Improve the quality of the deposit ex., tartrate, citrate
- Exhalant -Improve the plating rate ex., succinate, fluoride, glycinate
- Stabilizer-prevent the decomposition of plating bath.ex., thiourea, cations of Pb,Ca
- Buffer- Maintain the pH.ex., Sod.acetate, Sod.hydroxide

Electroless Ni Plating

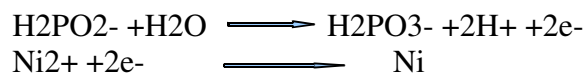
Pretreatment and activation of the surface

- Degreased by org. solvent
- Acid pickling-etching
- **Activation**
- Metals and alloys like Al, Cu, Fe can be directly plated without activation SS surface is activated by hot 50% dil H₂SO₄
- Mg alloy surface activated by giving thin coating of Zn and Cu
- Non-Metallic articles are activated by coating of Pd- Treated with SnCl₂ containing HCl followed by dipping in Pd. Chloride

Composition of the bath

Ni solution:	NiCl₂
Red agent :	Na Hypophosphite
Buffer :	Na. acetate
Complexing agent :	Na. Succinate
Cum Exhaltant	
pH :	4.5
Temp :	93C

Reactions



Factors influencing plating

- Addition of buffer is very essential as liberation of H^+ ion lowers the pH
- Plating starts at 70 C and reaches maximum at 93 C
- High temp above 93 C decomposes the bath
- Both Ni ions and Na hypophosphite are consumed during the redox reaction so they are replenished periodically
- Deposited metal is usually contaminated with O/R derivatives of reducing agent

Advantages

- Because of excellent throwing power, can be applied on irregular shape
- Free from pores
- Harder surface with better wear resistance due to the formation of Ni-P alloy
- Ni on Al enhances solderability
- Provide non-magnetic underlay in magnetic components

Applications

- Electronic appliances
- Heat treated electroless Ni-plated appliances finds applications in hydraulic compressors
- Domestic as well as automotive fields
- Coated polymers in decorative purposes
- Digital and electronic instruments for electromagnetic interference shielding purposes

Advantages of Electroless plating over Electroplating

- Does not require electrical power source
- Better throwing power and so intricate parts with irregular shapes can be uniformly coated
- Less porous
- Liberated hydrogen is not trapped in blind holes
- Applicable to conductors, semiconductors
- Needs no levelers to avoid uneven thickness
- Quality can be improved by addition of complexes and additive agents

ORGANIC COATINGS

- Organic Materials that are applied to protect or beautify a surface
- Important Organic Coatings are Paint, varnish, lacquers and enamels

Protection

Improve corrosion resistance by isolating the metallic structure from the corrosive environment
acts as inert barriers

Decoration

Yield desired colour and aesthetic appeal

The total annual cost for organic and metallic protective coatings is \$108.6 billion.

Protective value of Organic coatings

Depends on

- Chemical inertness to the corrosive environment
- Surface adhesion
- Impermeability to water, salts and gases
- Application method

PAINT

- Paint is a viscous, opaque, mechanical dispersion of one or more finely divided pigments and additives in vehicle and thinner

- When it is applied on to a metal surface, the thinner evaporates, while the vehicle undergoes slow oxidation forming a pigmented film

Requisites of good paints

- Fluid enough to spread easily
- High Covering power
- Easily applicable
- Form tough, uniform, adherent and impervious film
- Give a glossy film
- Dry quickly
- No crack formation on drying
- Must be stable
- Protect the surface from corrosion
- Resistance to water and corrosion
- Colour should be Stable -not fade

Constituents	Functions	Examples
Pigment: Solid substance Essential constituent Import color	Give color Provide strength / capacity <i>Protect film from UV rays by reflecting UV light</i> Improve weather resistance Improve impermeability	White: white Pb, zinc oxide, titanium oxide <i>Red: red Pb, ferric oxide chrome red</i> Green: chromium oxide Blue: Prussian blue Brown: brown umbre
Vehicle or drying oil: non-volatile liquid Film forming substance Holds all the ingredients in liquid suspension	Holds pigment particles on the metal surface Reduce the viscosity-applied easily on metallic surface <i>Form film by oxidation & polymerization reactions</i> <i>Improve adhesion of the film</i> Impart water repellency, toughness & durability	Glyceryl esters of higher mol.wt. fatty acids Linseed oil, castor oil, soya bean oil
Thinners or solvents: Volatile, easily evaporates after applied on the surface Driers: Oxygen carriers or catalysts	Reduce viscosity <i>Dissolve vehicle & additives</i> <i>Suspend the pigments</i> Increase penetration power of vehicle Increase the elasticity <i>Improve drying of oil film by oxidation, polymerization & condensation</i>	Turpentine, benzene,, dipentine, kerosene <i>Naphthenates, linoleates, borates & tungstates of metals(Pb, Zn, CO, Mn)</i> <i>Co sub: surface driers</i> <i>Pd sub: bottom driers</i> <i>Mn sub: thorough driers</i>

Extenders or fillers Fill the voids of the film Act as a carriers for pigments	Reduce the cost Increase the durability <i>Reduce the shrinkage & cracking</i> <i>Modify the shades of the pigments</i>	Low refractive indices in the materials <i>White coloured: Talc, asbestos, mica, slate powder, china clay</i>
Plasticizers To improve elasticity to the film	To minimize the cracks	Tricresyl phosphate, triphenyl phosphate
Antiskinning agent	<i>Preventing gelling and skinning of the paint film</i>	<i>Polyhydroxy phenols</i>

Types of oil

Drying oil

- Contains high percentage of conjugated fatty acid ester
- **Dry quickly by absorbing oxygen and used as a vehicle in paints**
- Ex., linseed oil, dehydrated castor oil

Semi-Drying oil

- low % of conjugated fatty acid ester
- Dry very slowly
- Used as blending agents with other drying oils to get desired film
- Ex: soya bean oil

Non-Drying oil

- Saturated fatty acid ester
- Do not dry even exposure to air
- Ex., sunflower oil

Mechanism of Drying of drying oil:

- The oil after applied on the surface absorbs oxygen of the air at the double bond, forming peroxides, diperoxides and hydroperoxides
- Peroxides isomerise, polymerise and condense to form a tough, coherent, hard, elastic, insoluble, infusible and highly cross-linked macromolecular film
- Final hardened product resembles a thermosetting resin in chemical nature

Special paints

Fire retardant paints: Protects surface against fire-Breaks down at high temp, produces non-inflammable gases which dilute the inflammable gases

Water repellent paints: Water and Weather proof paints- containing silicone resin

Temp indicating paints: Undergoes colour change at a specific temp

Failures of paints

Blistering: Blistering is the formation of bubbles resulting from localized loss of adhesion and lifting of the paint film from the underlying surface

Peeling: Spontaneous loss of ribbons or sheets of paint due to loss of adhesion

Cracking / Flaking: The splitting of a dry paint film through at least one coat, which will lead to complete failure of the paint. Early on, the problem appears as hairline cracks; later, flaking of paint chips occurs

Efflorescence: The formation of crusty, white salt deposits, leached from mortar or masonry as water passes through it.

Mildew: The formation of brown, black or gray spots or blotches on the surface of paint due to the presence of fungi that feed on the paint film and other organic matter.

Chalking: Progressive powdering of the paint film due to destruction of binder by continuous exposure to light

Colour change of the paint film: Chemical effect of atm gases on the paint

Blistering underneath of paint film: Results in galvanic corrosion