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NARSIMHA REDDY
ENGINEERING COLLEGE
UGC AUTONOMOUS ACCREDITED BY NBA&NAAC WITH A-GRADE

CHEMISTRY

UNIT I

WATER & ITS TREATMENT

- BY R SATYAVATHI

Sources of water

- Surface water :-The water which comes from surface through rain. eg :- rain water, river water & sea water.

- Underground water :- This water comes from rain that falls on earths surface & then goes into the ground water & travel down the impervious (cracks) layers of earth, thus forming ground water. eg :- spring water & well water.

HARD WATER	SOFT WATER
Does not form lather with soap easily	Forms lather with soap easily
Contains dissolved salts of Ca & Mg	Does not contain dissolved salts of Ca & Mg
More wastage of time & fuel as boiling temp. of water gets increased due to impurities	Less wastage of time & fuel
More consumption of soap by hard water	Less consumption of soap by soft water

Hardness of water

- Hardness is the soap consuming capacity of water
- Hardness of water is due to the presence of Ca and Mg salts in it. Other ions responsible for hardness are Al^{3+}, Fe^{3+} and Mn^{2+}
- If Ca and Mg salts are present in water then they react with the soluble sodium soap to form insoluble salts calcium and magnesium.
- $2C_{17}H_{35}COONa + CaSO_4 \text{---}\rightarrow (C_{17}H_{35}COO)_2Ca + Na_2SO_4$

  Sodium stearate Insoluble salt
- $2C_{17}H_{35}COONa + MgCl_2 \text{---}\rightarrow (C_{17}H_{35}COO)_2Mg + 2NaCl$

Types Of Hardness

TEMPORARY

PERMANENT

Temporary Hardness

- Caused by the presence of dissolved bicarbonates of Ca, Mg and. This hardness is also known as alkaline hardness.

- Easily removed by heating :

- $Ca(HCO_3)_2 \xrightarrow{\text{Heat}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$

- $Mg(HCO_3)_2 \xrightarrow{\text{Heat}} Mg(OH)2 \downarrow + CO_2 \uparrow$

Permanent Hardness

- Due to the presence of sulphates and chlorides of Ca & Mg
- Cannot be removed simply by boiling.
- Special methods like lime soda process, zeolite process, ion-exchange method are used for the removal of permanent hardness.

Boiler feed water

- For steam generations, boilers are used
- if hard water is fed to the boiler, various problems are faced by boiler :

- ➢ Scale and Sludge formation
- ➢ Priming and Foaming
- ➢ Boiler corrosion
- ➢ Caustic embrittlement

Sludge

FORMATION:

- Where flow of water is slow
- At colder region
- By substances which have greater solubility in the hot water.
- $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

DISADVANTAGES:

- Poor conductor of heat hence more consumption of time and fuel.
- Disturbs functioning of boiler & settles in the regions of poor water circulation.

PREVENTION :

- By using soft water
- By using blow down pipe operation .

Scale

❖ FORMATION :

➢ Decomposition of $Ca(HCO_3)_2$:

- $Ca(HCO_3)_2 \longrightarrow \underset{\text{Soft Scale}}{CaCO_3} + H_2O + CO_2$
- $CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2$

➢ Deposition of $CaSO_4$:

- Soluble in cold water
- As temp. ↑ solubility of $\underset{\text{hard scale}}{CaSO_4}$ ↓

➢ Hydrolysis of Mg salts

- $MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$

➢ Presence of (SiO_2)

Scale

DISADVANTAGES

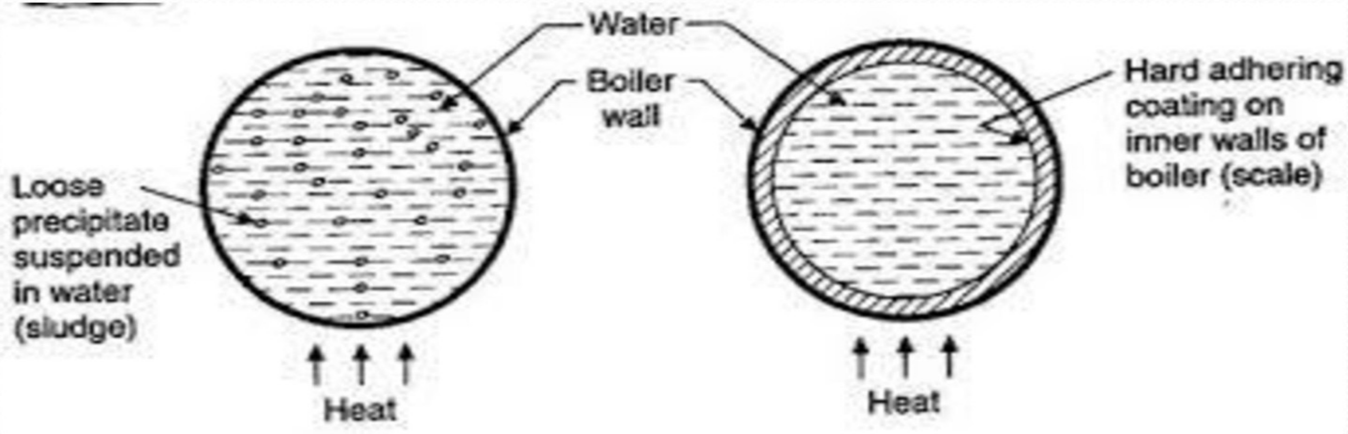
- Fuel Wastage
- Lowering of boiler safety
- Decreased efficiency
- Danger of explosion

Removal

- Using wire brush
- By using chemicals :
- $CaCO_3$ scales by 5-10% HCl
- $CaSO_4$ scales by EDTA
- Blow down pipe operation
- By giving thermal shocks

Sludge & Scale

- Continous evaporation of water takes place & conc. of dissolved salts gets increased & at saturation point forms ppts. on the inner walls of the boiler.
- Sludges : If loose & slimy ppts formed.
- Scales : If sticky, hard & adhernt coat formed.
-
- Sludge Scale



Scale

- **Prevention**
- External Treatment
  - By using soft water
- INTERNAL TREATMENT
  - Colloidal conditioning :
    - Addition of organic substances such as tannin, Agar- Agar
  - Phosphate conditioning :
    - $CaCl_2 + Na_3PO_4 \longrightarrow$ Calcium phosphate $+ 6NaCl$
  - Carbonate conditioning
    - $CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$
  - Calgon conditioning
    - $CaSO_4 +$ calgon $\longrightarrow$ Soluble complexes of Ca ions
  - Treatment with sodium aluminate :
    - $NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$

Caustic Embrittlement

- formation of brittle and incrystalline cracks in the boiler shell due to the accumulation of caustic substances

- Cause

- Presence of alkali-metal carbonates and bicarbonates in feed water
- presence of sodium sulphate.
- Sodium carbonate is used in softening of water by lime soda process, due to this some sodium carbonate may be left behind in the water.

❖ Process

- Na_2CO_3 used for softening of water & some of which remain unreacted

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

- As Conc. of NaOH increases, water flows into minute hair cracks by capillary action.
- As water evaporates, conc. of NaOH increases further and react with iron of boiler, (thereby dissolving Iron of boiler as Sodium ferroate), hence cause Embrittlement.
- This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail.etc.

❖ prevention :

- Use of Na_3PO_4 instead of Na_2CO_3
- By adding tanin & lignin that blocks the hair cracks
- By adding $NaSO_4$ that also blocks the cracks

Internal Treatment of Water

Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds is called internal treatment of the boiler feed water. Internal treatment can be done following types.

Colloidal conditioning:

The addition of organic substances such as Kerosene, tannin, Gel. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

Internal Treatment of Water

Phosphate conditioning: The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$$

$$3MgSO_4 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3Na_2SO_4$$

Generally three types of Phosphates are employed.

i. Trisodium Phosphate (Na_3PO_4): is too alkaline used for treat to too acidic water.

ii. Disodium Phosphate (Na_2HPO_4): is weakly alkaline used for treat to weakly acidic water.

iii.Sodium dihydrogen Phosphate ($Na\ H_2PO_4$): is too acidic used for treat to too alkaline water.

Internal Treatment of Water

Calgon conditioning: Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $\mathrm{CaSO4}$. Calgon = Sodium hexametaphosphate = $\mathrm{Na2\ [Na4\ (PO3)6]}$

$$\mathrm{Na2\ [Na4\ (PO3)6]} \rightarrow \mathrm{2Na+} + \mathrm{[Na4P6O18]\ -2}$$

$$\mathrm{2CaSO4} + \mathrm{[Na4P6O18]\ -2} \rightarrow \mathrm{[Ca2\ P6O18]\ -2} + \mathrm{2Na2SO4}$$

Softening Methods

The following methods are used :

- Lime soda Process
- Zeolite softening process
- Ion exchange process

Ion Exchange or De-ionization or De-mineralisation process

- Hard water is allowed to pass through ion exchangers when soft water, free from all the minerals and hardness causing as well as the other ions is obtained.

- Types
  - Cation Exchange Column represented with its H^+ ions
  - Anion Exchange Column represented with its OH^- ions

Ion exchange process

Ion exchange process is also known as demineralization process. Ion- Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties.

- Resins with acidic functional group are capable of exchanging H^+ ions with other cations.
- Resins with basic functional groups are capable of exchanging OH^- ions with other anions.

Resins are classified as:

- Cation Exchange Resins
- Anion Exchange Resins.

Ion exchange process

➢ Cation Exchange Resins:

Cation exchange resins are styrene divinylbenzene co-polymers, which on sulphonation (or) carboxylation, which contains –COOH, –SO3H functional groups which responsible for exchanging their hydrogen ions with cations in water.

➢ Anion Exchange Resins:

Anion exchange resins are Phenol formaldehyde (or) amine formaldehyde copolymers, which contains amino or basic functional groups which responsible for exchanging their OH^- ions with anions in water.

Ion exchange process

Process:

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove Ca+2 and Mg+2 ions and exchange equivalent amount of H+ ions.

Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH− ions.

Thus by passing hard water through cation hardness is observed by the following reactions. H + and OH− ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

$$H + + OH^{-} \rightarrow H2O$$

The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

Ion exchange process

Cation Exchange Resins:

$2RH + Ca(HCO)_2 \rightarrow R_2Ca + H_2CO_3$

$2RH + Mg(HCO)_2 \rightarrow R_2Mg + H_2CO_3$

$2RH + CaCl_2 \rightarrow R_2Ca + 2HCl$

$2RH + MgCl_2 \rightarrow R_2Mg + 2HCl$

$2RH + MgSO_4 \rightarrow R_2Mg + H_2SO_4$

$2RH + CaSO_4 \rightarrow R_2Ca + H_2SO_4$ (RH = Cation exchange resin)

Anion Exchange Resins:

$ROH + HCl \rightarrow RCl + H_2O$

$2ROH + H_2SO_4 \rightarrow R_2SO_4 + 2H_2O$

$ROH + H_2CO_3 \rightarrow RHCO_3 + H_2O$(ROH = anion exchange resin)

Process

Cation Exchange column :

$$\underset{\text{Cation exchange resin}}{2RH^{+}} + \underset{\text{H. W.}}{Ca^{+2}} \longrightarrow \underset{\text{Cation exchange resin}}{R2Ca^{+2}} + \underset{\text{S. W.}}{2H^{+}}$$

Anion Exchange column :

$$\underset{\text{Anion exchange resin}}{R'OH^{-}} + \underset{\text{H. W.}}{Cl^{-}} \longrightarrow \underset{\text{Anion exchange resin}}{R'Cl^{-}} + \underset{\text{S. W.}}{OH^{-}}$$

$$\underset{\text{Anion exchange resin}}{2R'OH^{-}} + \underset{\text{H. W.}}{SO4^{-2}} \longrightarrow \underset{\text{Anion exchange resin}}{R_2'SO4^{-2}} + \underset{\text{S. W.}}{2OH^{-}}$$

Regneration:

CationExchange column :

$$\underset{\text{Saturated Cation exchange resin}}{R_2Ca^{+2}} + \underset{\text{dil. acidic sol.}}{2H^{+}} \longrightarrow \underset{\text{Regenerated Cation exchange resin}}{2RH^{+}} + \underset{\text{washings}}{Ca^{+2}}$$

Anion Exchange column :

$$\underset{\text{Saturated anion exchange resin}}{R_2'SO4^{-2}} + \underset{\text{dil. Basic sol.}}{2OH^{-}} \longrightarrow \underset{\text{Regenerated Cation exchange resin}}{2R'OH^{-}} + \underset{\text{washings}}{SO4^{-2}}$$

POTABLE WATER

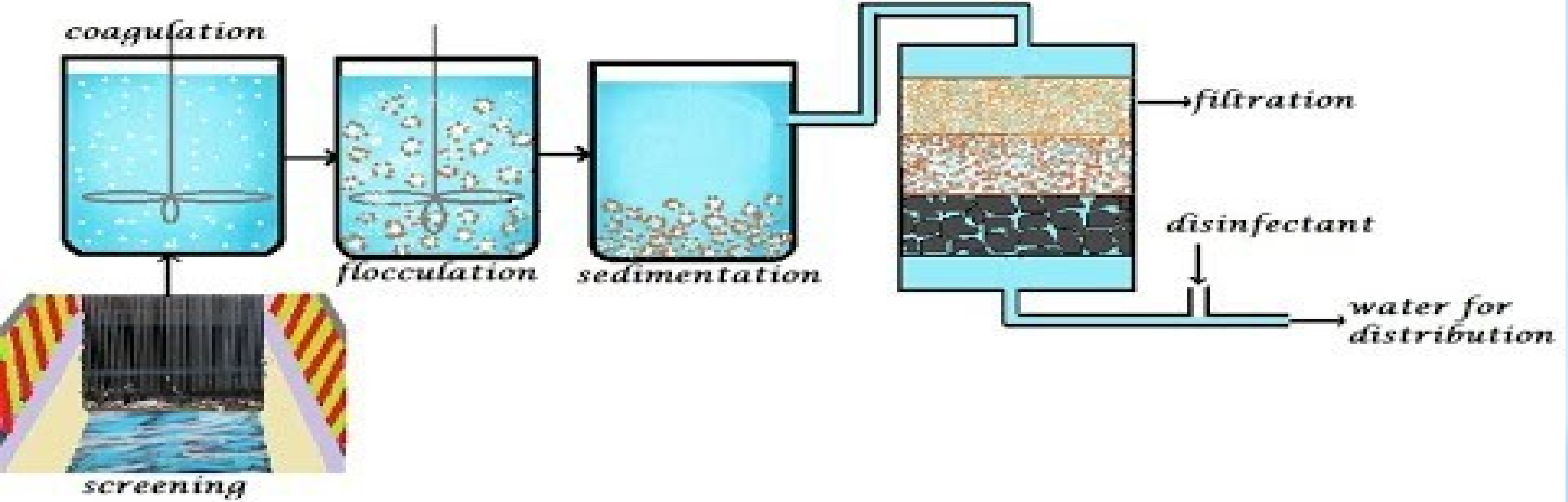
Potable water:

Water which is fit for drinking is called potable water.

Specification for drinking water

- It should be bacteria free
- It should not contain any suspended impurities
- It should not have bad taste.
- It should not contain toxic materials such as lead, arsenic, chromium and copper.
- pH should be in the range 7 to 8.5
- It should be slightly alkaline
- It should be free from dissolved gases like H_2S, CO_2 etc.
- Its turbidity should be less than 10 ppm.
- It should be cool
- It should be reasonably soft.

DRINKING WATER TREATMENT



Steps involved in the treatment of Potable water

Treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria. The following stages are involved in purification.

1. **Screening**: The water is passed through screens having larger number of holes; it retains floating impurities like wood pieces, leaves, heaver objectives etc.

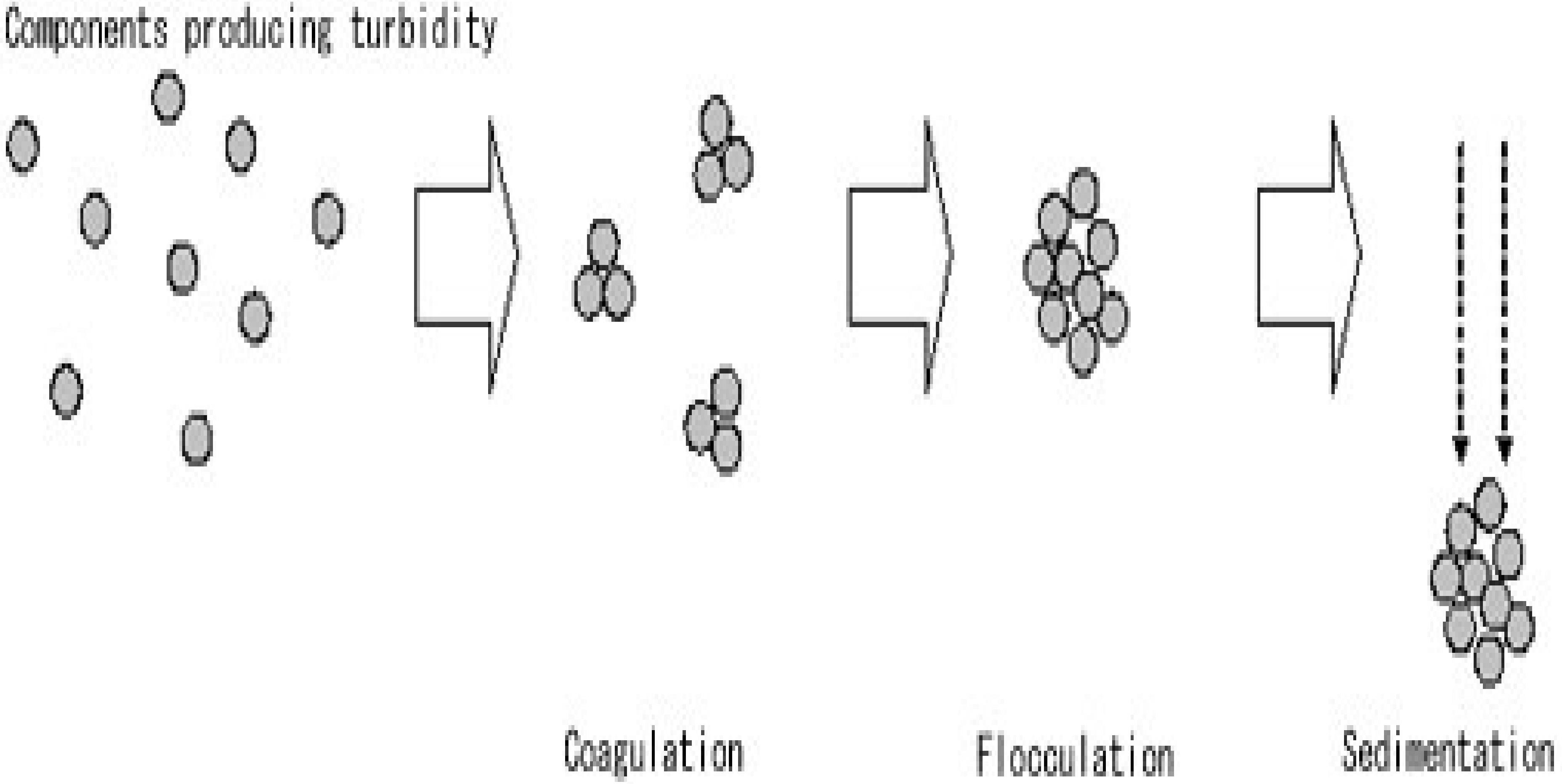
2. **Coagulation**: Coagulants like alum, sodium aluminates and Aluminum sulphate are added which produce gelatinous precipitates called flock. Flock attracts and helps accumulation of the colloidal particles resulting in setting of the colloidal particles.

Steps involved in the treatment of Potable water

Sedimentation: Water is allowed to stand for few hours so that the suspended particles will det settle at the bottom of the tank.

Filtration: Filtration helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually sand filters are employed. In this filtration fine sand layer on the top supported by coarse sand layer, which is supported by gravel.

Disinfection of water by sterilization: The process of destroying the harmful bacteria is known as sterilization or disinfection.


Components producing turbidity
Coagulation
Flocculation
Sedimentation

Disinfection of Potable water

- **By Ozonization:** Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen.

$$O_3 \rightarrow O_2 + [O] \text{ nascent oxygen}$$

The nascent oxygen is a powerful oxidizing agent and kills the bacteria.
Disadvantages: This process is costly and cannot be used in large scale, due to unstable of ozone cannot be stored for long time.

- **By Chlorination:** The process of adding chlorine to water is called chlorination. Chlorination can be done by the following methods.

Disinfection of Potable water

By adding Chlorine gas: Chlorine gas is a very good disinfectant, which can be bubbled in the water. In this process calculated amount of chlorine gas is passed in order to destroy the pathogenic bacteria is called chlorination. Chlorine is also reacts with water and generates hypochlorous acid and nascent oxygen, which acts a powerful oxidizing agent and kills the bacteria.

$$Cl_2 + H_2O \rightarrow HOCl \text{ (Hypochlorous acid)} + HCl$$

$$HOCl \rightarrow HCl + [O] \text{ nascent oxygen}$$

By adding Chloramine: When chlorine and ammonia are mixed in the ratio 2:1 a compound chloramine is formed.

$$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl \text{ Chloramin}$$

Disinfection of Potable water

$ClNH_2 + H_2O \rightarrow NH_3 + HOCl$ (Hypochlorous acid)

$HOCl \rightarrow HCl + [O]$ nascent oxygen

Chloramine compounds decompose slowly to give nascent oxygen which will be act as good disinfectant than the Chlorine.

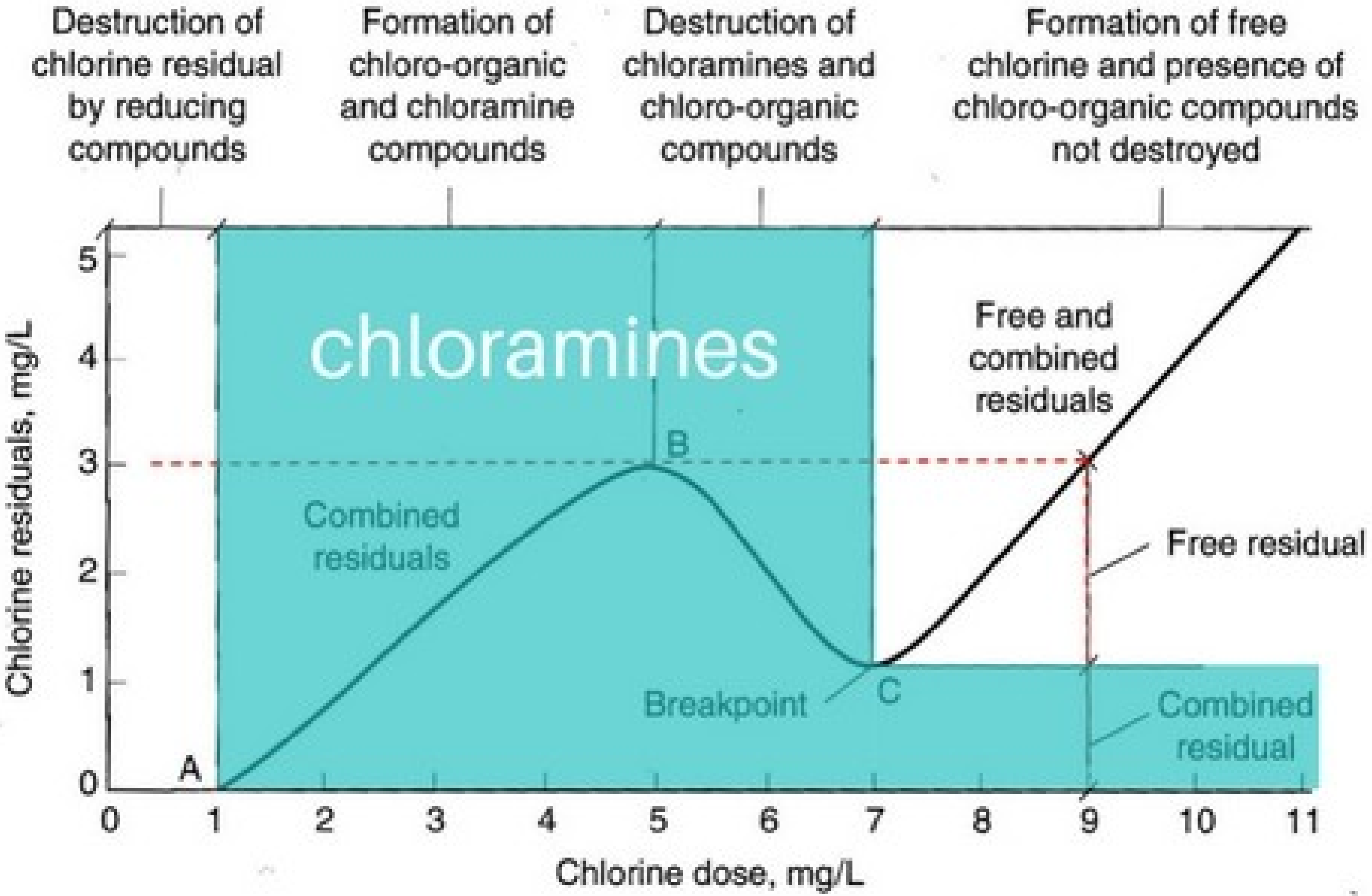
Chloramine gives good taste to the treated water.

BREAK POINT CHLORINATION

Break-point chlorination: The amount of chlorine required to kill bacteria and to remove organic matter is called breakpoint chlorination.

The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph as shown below which gives the break-point chlorination.

From graph it is clear that: ‘a’ gms of chlorine added oxidizes reducing impurities of water.
‘b’ gms of chlorine added forms chloramines and other chloro compounds.
‘c’ gms of chlorine added causes destruction of bacteria.
‘d’ gms of chlorine is residual chlorine. ‘c’ gms is the break point for addition of chlorine to water.
This is called break- point chlorination.


Destruction of chlorine residual by reducing compounds
Formation of chloro-organic and chloramine compounds
Destruction of chloramines and chloro-organic compounds
Formation of free chlorine and presence of chloro-organic compounds not destroyed
chloramines
Free and combined residuals
Combined residuals
B
Free residual
Breakpoint
C
Combined residual
A
Chlorine residuals, mg/L
0
1
2
3
4
5
0
1
2
3
4
5
6
7
8
9
10
11
Chlorine dose, mg/L

BREAK POINT CHLORINATION

Advantages of breakpoint chlorination:

➢ It removes bad taste, colour, oxidizes completely organic compounds, ammonia and other reducing impurities ➢ It destroys completely (100%) all disease producing bacteria.

➢ It prevents growth of any weeds in water.

Battery:

A battery is an arrangement of several electrochemical cells connected in series that can be used as a source of direct electric current

Cell: contains one anode and one cathode

Battery contains several anodes and several cathodes

Types of batteries

Primary batteries:

Not rechargeable

Electrode reactions cannot be reversed

Examples : Dry cell, mercury cells, lithium cells

Secondary batteries:

Can be recharged

Electrode reactions can be reversed

Examples: Lithium ion cell, lead acid battery, nickel cadmium battery

Lithium cells

Lithium cells with solid cathode

Anode: Li

Cathode: MnO2

Electrolyte: LiBF4 salt in a solution of propylene carbonate & dimethoxyethane

Lithium cells with liquid cathode

Anode: Li

Cathode: SOCl2

Electrode: SOCl2

Lead-Acid battery

During discharging

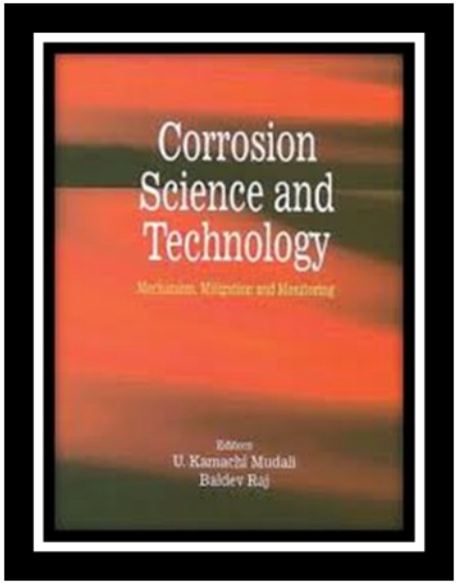
Lead acid battery acts as voltaic cell

During charging

Lead acid battery acts as electrolytic cell

ENGINEERING CHEMISTRY

Corrosion and its control



Corrosion Science and Technology

Mechanisms, Mitigation and Monitoring

Editors
U. Kamachi Mudali
Baldev Raj

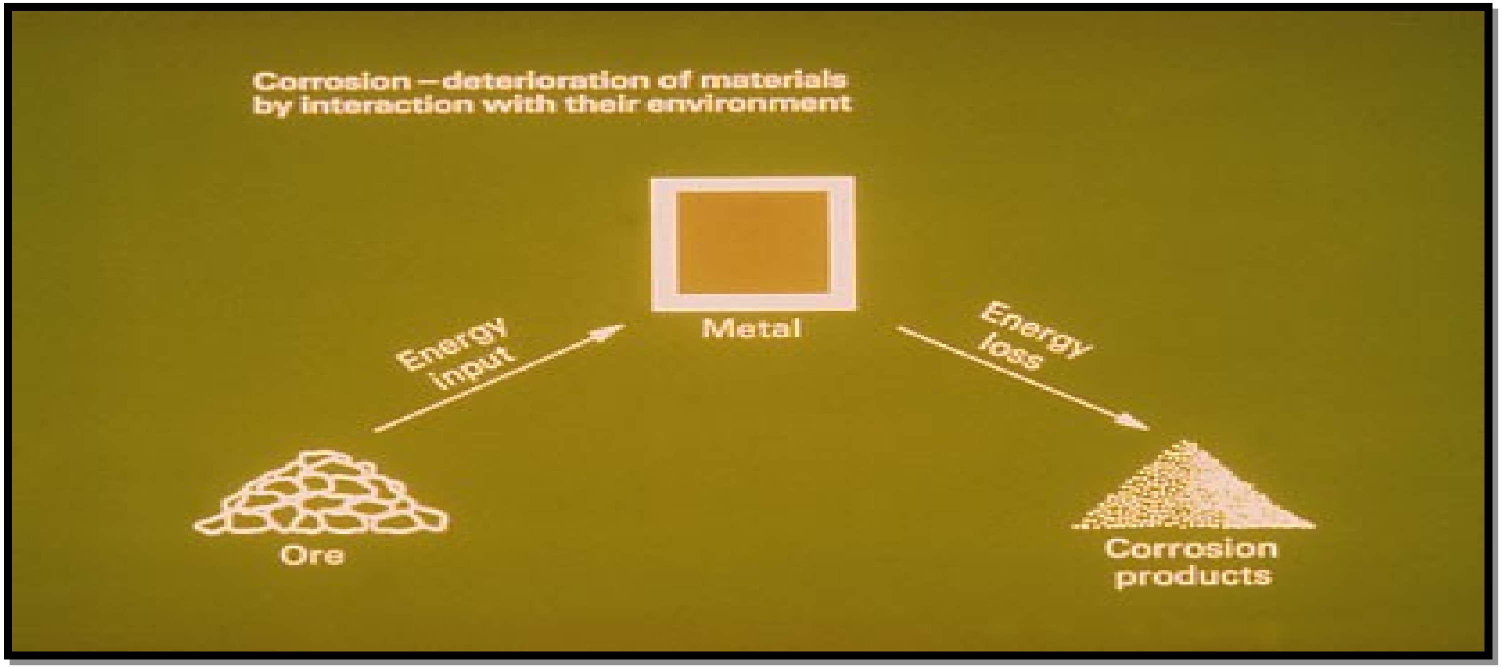
CORROSION AND ITS CONTROL

- INTRODUCTION
- CAUSES OF CORROSION
- THEORIES OF CORROSION
- CORROSION REACTIONS
- FACTORS EFFECTING THE CORR
- TYPES OF CORROSION
- CORROSION CONTROL METHODS

INTRODUCTION

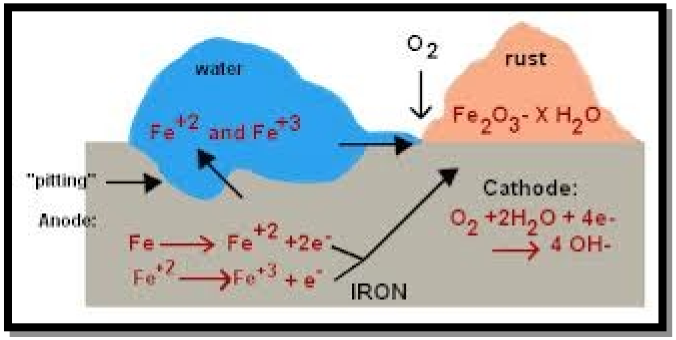
- Destruction of a metal by chemical or electrochemical reaction with its environment.
- Physical or mechanical wearing away of a metal is not called corrosion but is called erosion
- If corrosion and erosion take place together the destruction of the metal takes place very much faster
- Corrosion is an unintentional attack on a material by reaction with a surrounding medium
- The corrosion problem should be very seriously considered in all those cases where the structure or the equipment is meant to last many years say 20 years…

Definition of Corrosion

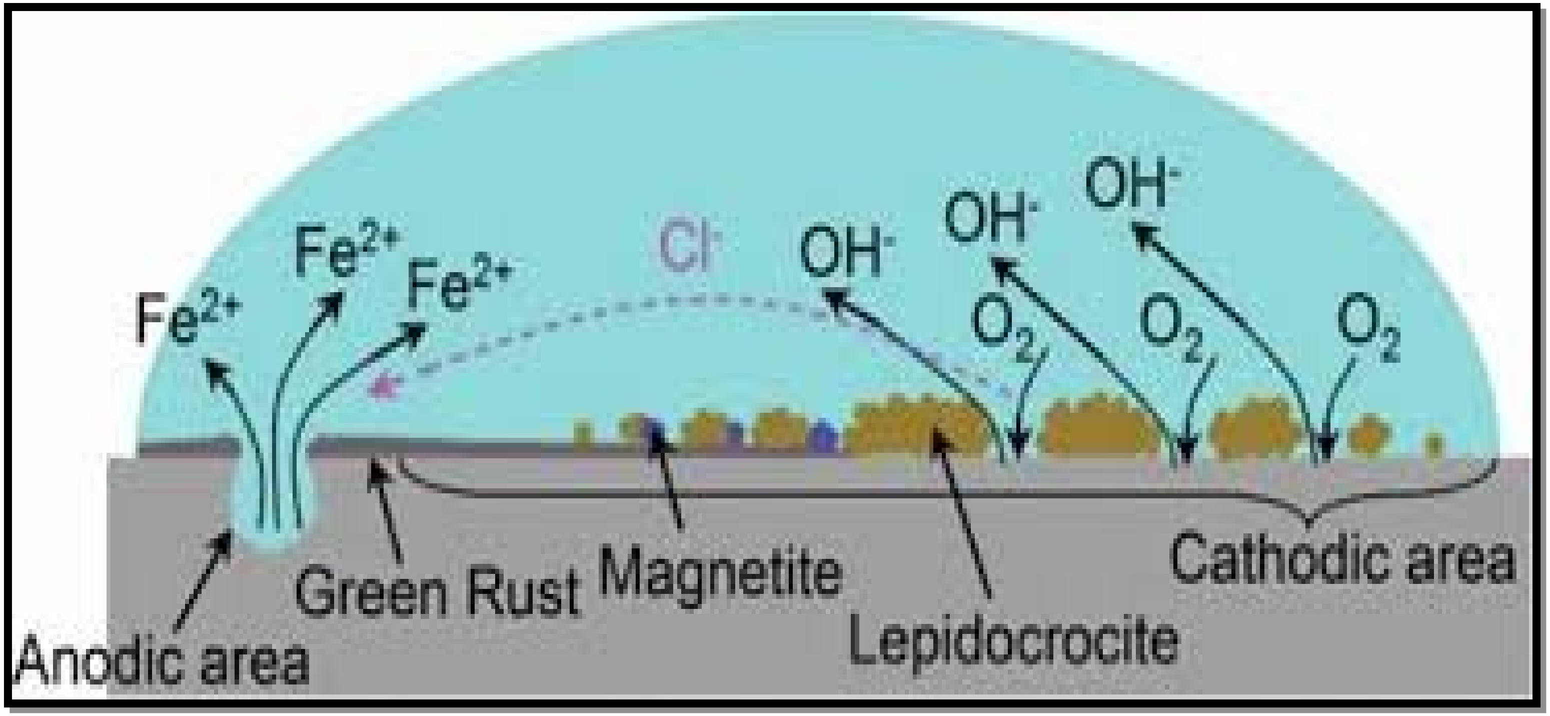


Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.

Rusting of iron



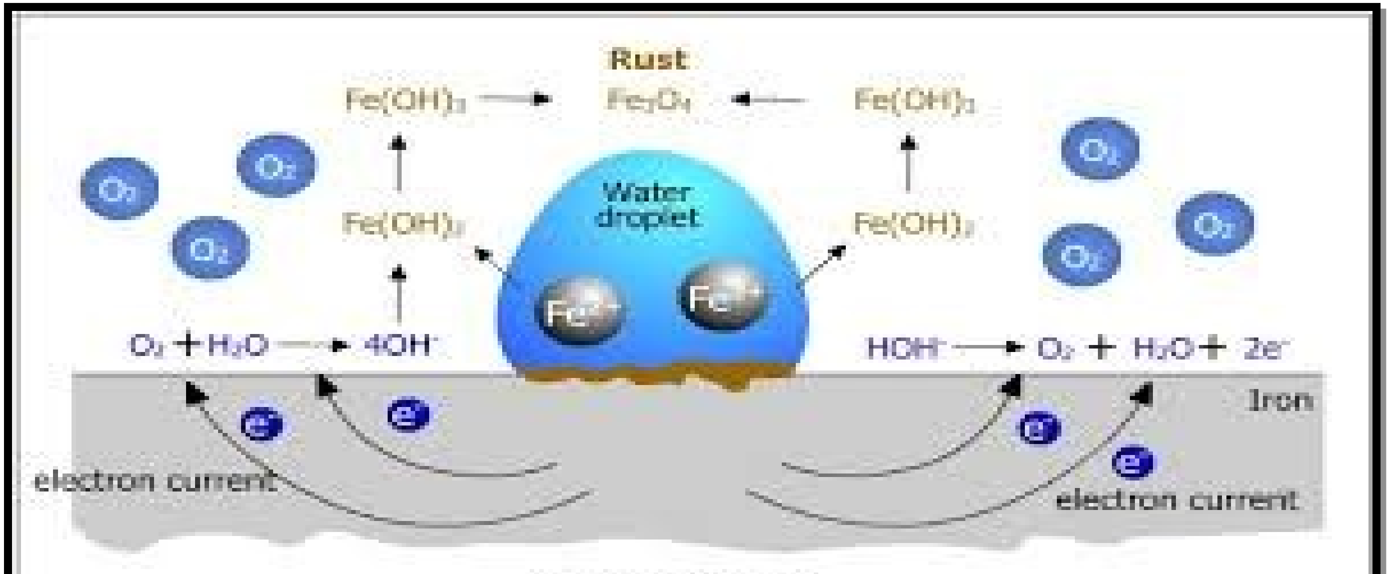
Formation of green rust



CAUSES OF CORROSION

- The chemical combined state of the metal is known as **“ore”**
- The ore has low energy in its thermodynamical state.
- The extracted metal has high energy ,thermodynamically unstable .
- Metal converts itself into stable state by reacting with the environment and undergoes corrosion.
- The corroded metal is thermodynamically stable.

Formation of rust

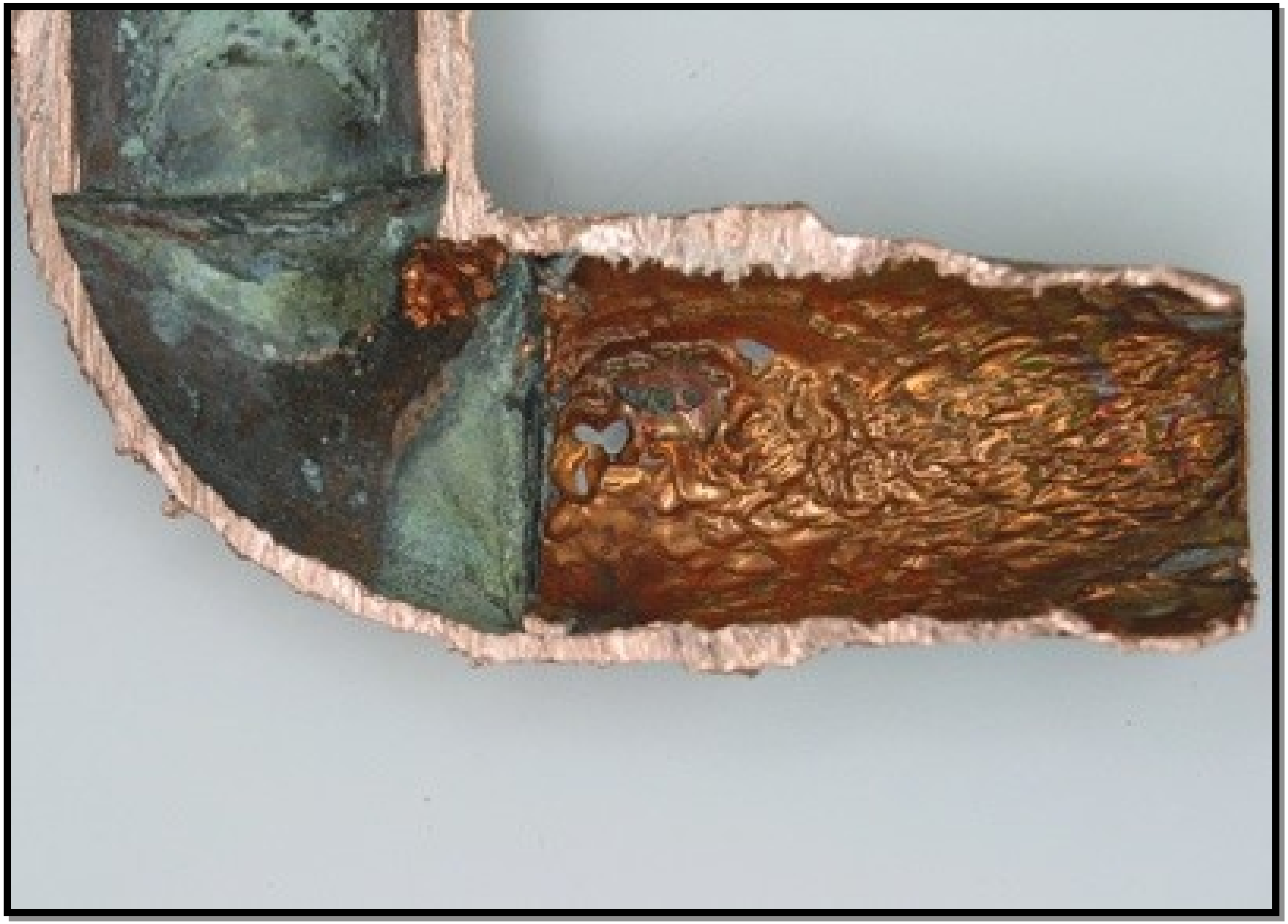


Formation of Rust.

Effects or disadvantages of corrosion

- The valuable metallic properties like conductivity,malleability, ductility etc are lost due to corrosion.
- Life span of the metallic parts of the machineries is reduced.
- The process of corrosion is very harmful and is responsible for the enormous wastage of metal in the form of its compound.
- The failure of the machinery takes place due to lose of useful properties of metals.
- The approximate estimate of loss of metal due to corrosion is 2 to 2.5 billion dollars per annum all over the world.


1 mm



TYPES OF CORROSION

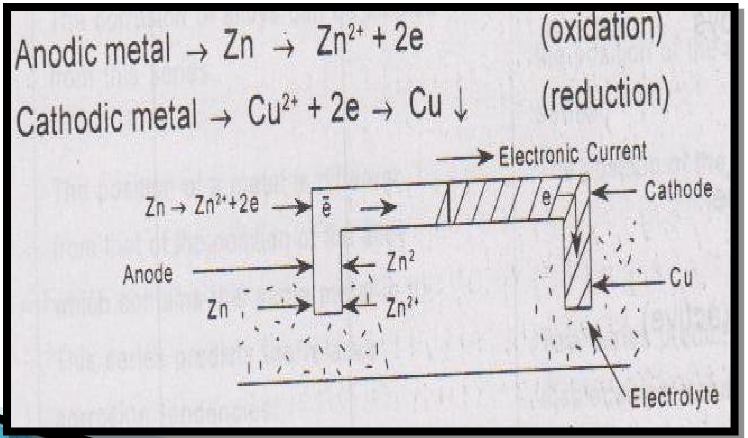
Different types of electrochemical corrosions are

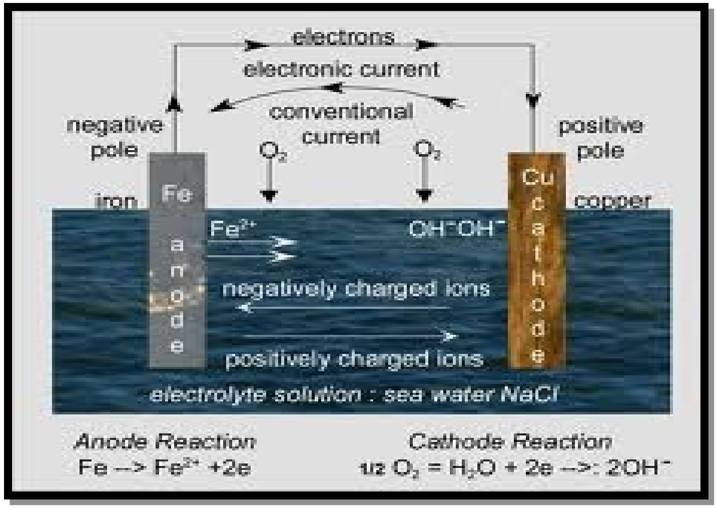
- Galvanic corrosion
- Pitting corrosion
- Intergrannular corrosion
- Water line corrosion

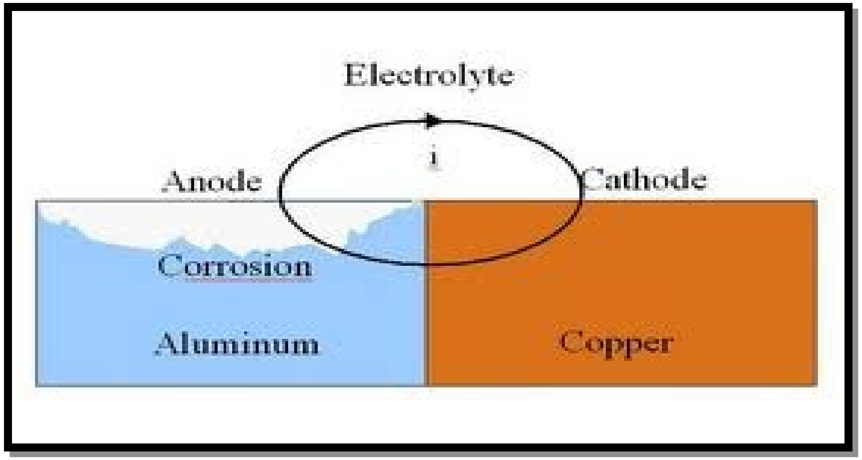
Galvanic corrosion

- This corrosion occurs when different metals are in contact and exposed to corrosive atmosphere.

- The metal which has higher electrode potential value will form anode and undergoes corrosion. Example: Zn-Cu galvanic cell zinc behaves as anode and corrosion occurs, copper behaves as cathode and protected.

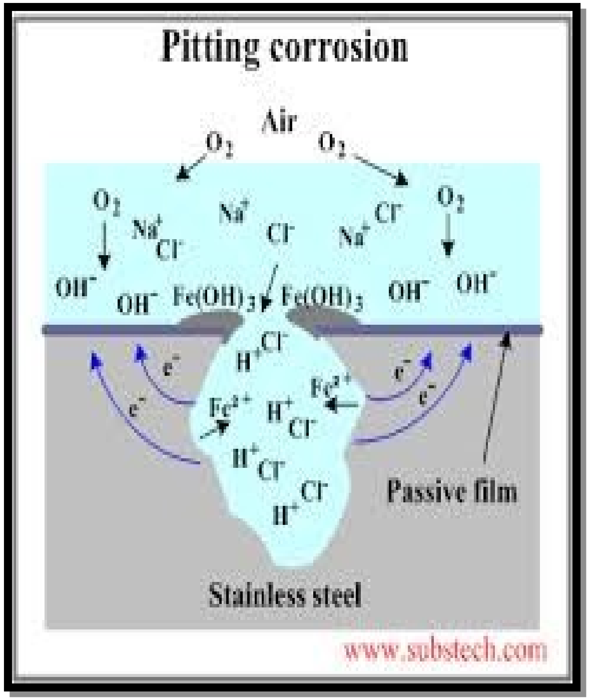


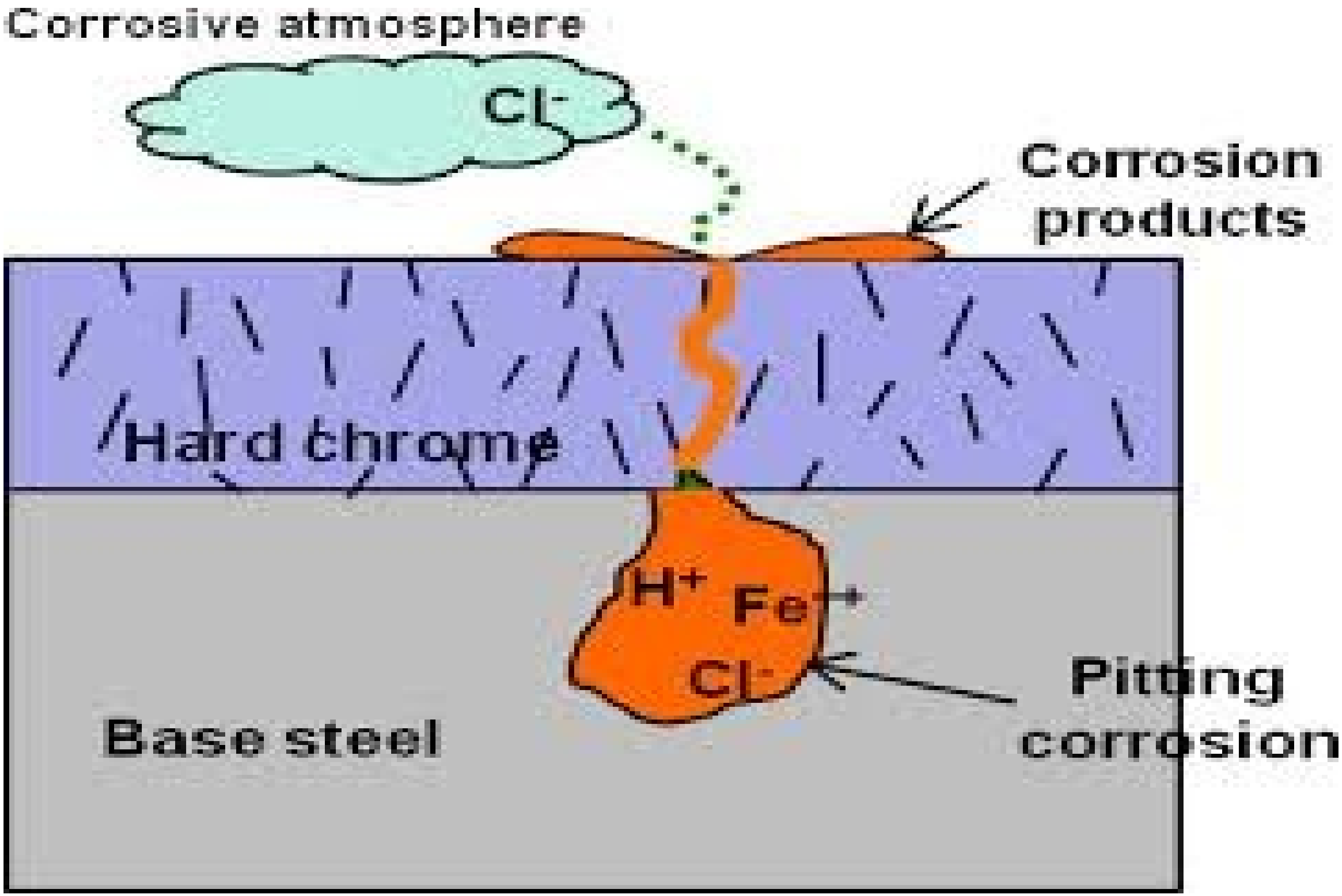



Electrolyte
i
Anode
Cathode
Corrosion
Aluminum
Copper

Pitting corrosion

- When corrosion starts on a metal surface at certain spots they become less open to oxygen with the result that corrosion proceeds faster at those very spots making deeper and deeper cavities.
- Pitting corrosion can be explained on the basis of differential aeration.
- The pit created becomes deeper, its bottom becomes less open to oxygen which makes it more anodic.
- The part which has higher oxygen concentration is cathodic.




Corrosive atmosphere
Cl^-
Corrosion products
Hard chrome
H^+
Fe^{++}
Cl^-
Pitting corrosion
Base steel

Water line corrosion

- The concentration of oxygen dissolved in water is greater at the surface than deeper down. This causes formation of a concentration cell.
- Anode is the lower portion .
- Cathode is at the water level.
- Due to the poor conductivity of water the ions just below the water level are available for reaction, the metal corrodes just below the water level.

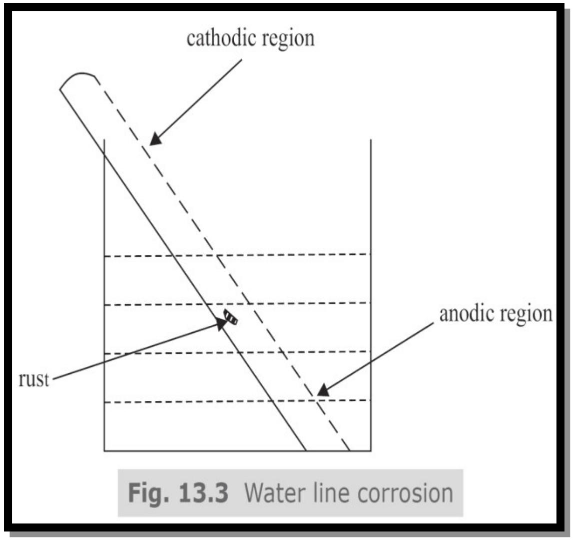


Fig. 13.3 Water line corrosion

Theories of corrosion

THEORIES OF CORROSION

- In atmospheric corrosion the metals tend to revert to the states in which they occur in nature.

- Several theories of corrosion have been proposed from time to time..

- The three theories are
  i) ACID THEORY
  ii) CHEMICAL CORROSION (**DRY CORROSION**)
  iii) ELECTROCHEMICAL CORROSION (**WET CORROSION**)

ACID THEORY

Acid theory of corrosion considers acid to be the main cause.

Rusting takes place faster in acid solutions than in neutral or basic solutions.

Oxygen and water are necessary for rusting of iron.

This is not true for all the metals like Zn etc..

Rate of corrosion in absence of Carbon di oxide is also seen.

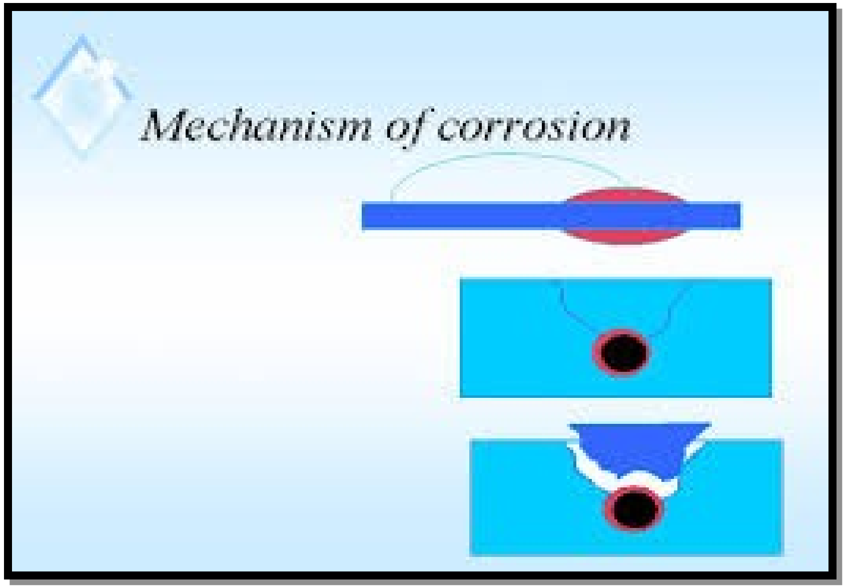
Dry corrosion or chemical corrosion

- The direct chemical reaction of environment/atmospheric gases or inorganic liquids with metal surfaces .
- There are three types of chemical corrosion

i) Oxidation corrosion

ii) Corrosion by other gases

iii) Liquid metal corrosion



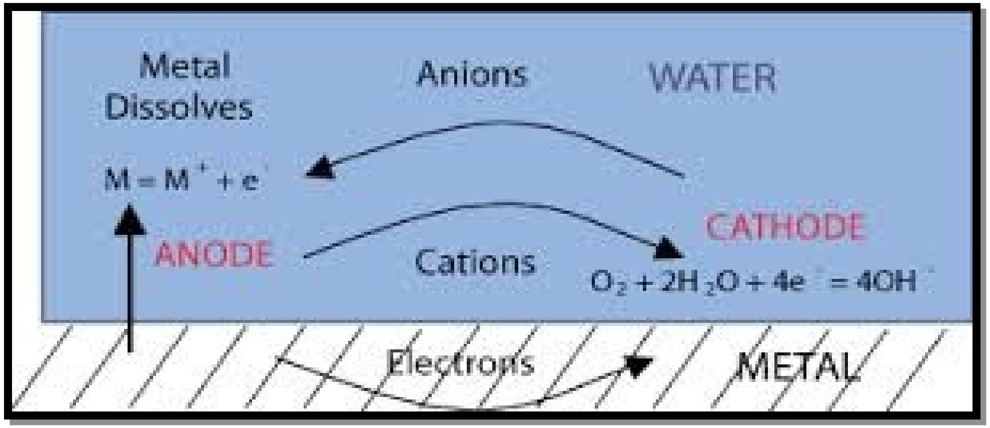
(1.) Oxidation Corrosion: This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture.

Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).

$$M \rightarrow M_2^{+} + 2e^{-} \text{ (Oxidation)}$$

$O_2 + 2e^{-} \rightarrow 2O_2^{-}$ (Reduction)

$M + O_2 \rightarrow M_2^{+} + 2O^{2-}$ (Metal oxide)



Mechanism:-

1. When temp increases the metal undergoes oxidation and losses e^-

$$2M \rightarrow 2M^{+n} + 2ne^-$$

Metal Ion

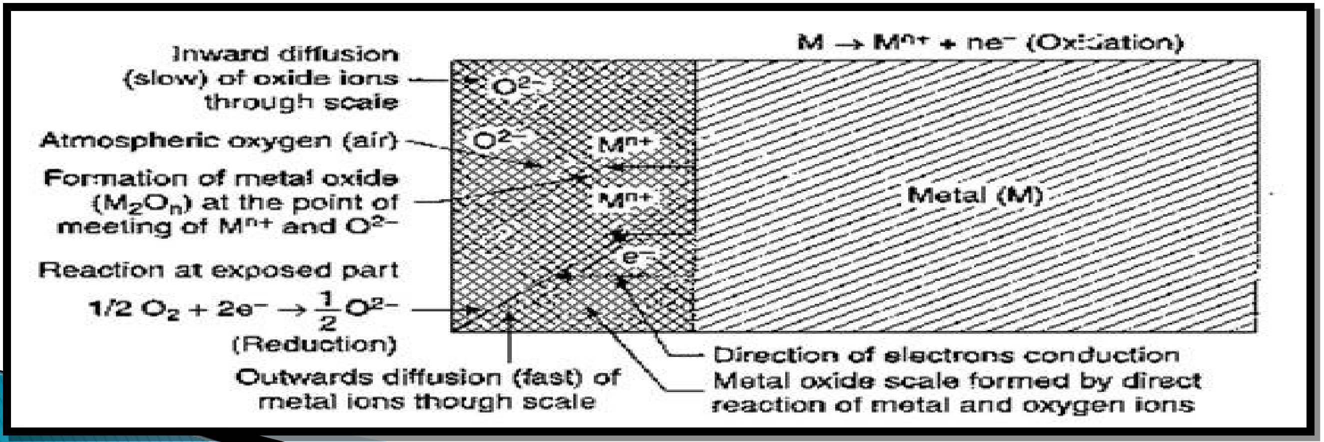
2. Electron are gained by the oxygen molecules forms oxide ions

$$nO_2 + 4ne^- \rightarrow 2n\, O^{2-}$$

Oxide Ion

3. Scale of metal oxide formed $2M + nO_2 \rightarrow 2M + 2n\, O^2$

Metal Oxide



2.) **Corrosion due to other gases:** This type of corrosion is due to gases like SO_2, CO_2, Cl_2, H_2S, F_2 etc. In this corrosion, the extent of corrosive effect 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 films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous does not allow the penetration of corrosive gases.

$Ag + Cl_2 \rightarrow 2AgCl$ (protective film)

(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.
Ex. In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale. Fe (steel) + H_2S FeS (porous)

3.) **Liquid metal corrosion:** This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.
Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

Wet or Electrochemical corrosion

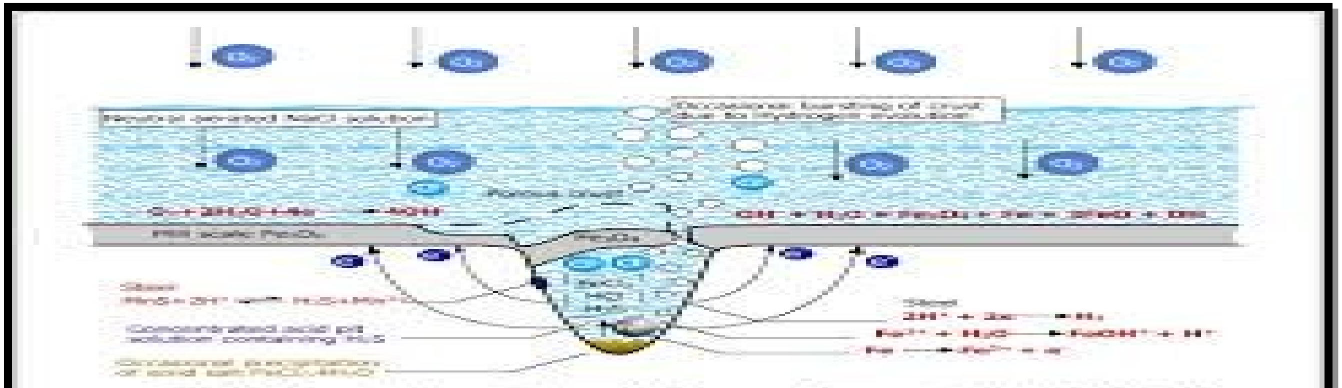
- The electrochemical corrosion occurs when

  i) a conducting liquid is in contact with a metal.

  ii) when two dissimilar metals or alloys are immersed partially in the solution.

- Corrosion occurs due to the presence of anodic and cathodic areas.

- At anode oxidation reactions takes place
- At cathode reduction reactions takes place



Electrochemical reactions that occur when a pit is initiated at sulphide inclusion in a carbon steel.

- Occurs when aqueous solution or liquid electrolytes are present

- Wet corrosion takes place in environments where the relative humidity exceeds 60 %.

- Wet corrosion is most efficient in waters containing salts, such as NaCl (e.g. marine conditions), due to the high conductivity of the solution.

Mechanism Of Electrochemical Corrosion

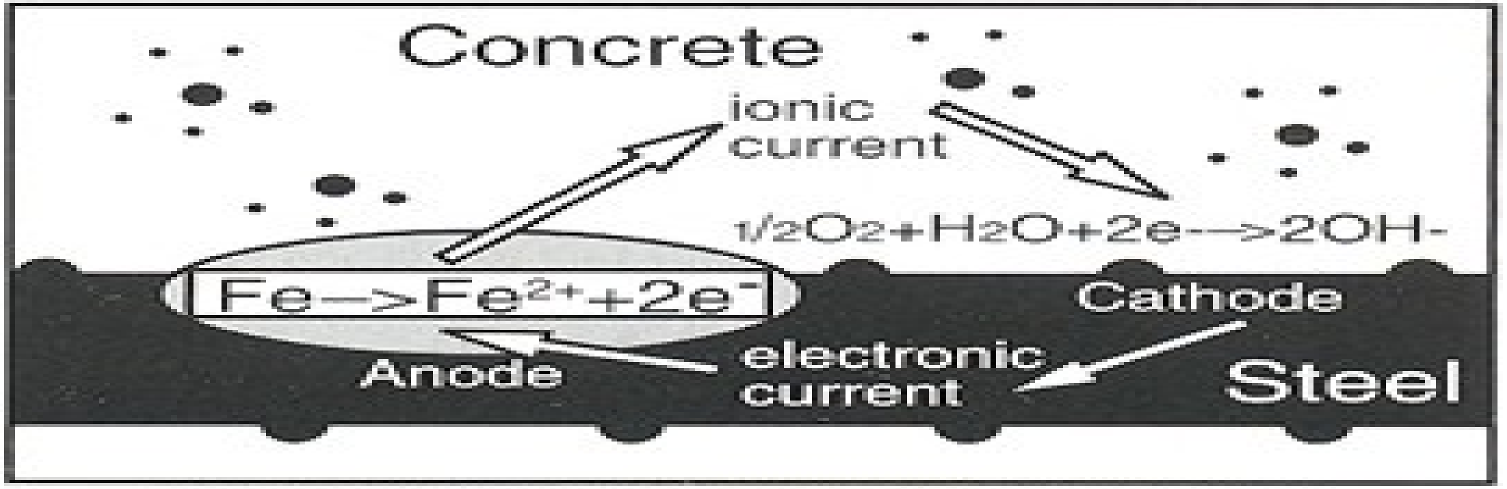


Figure 1: The anodic and cathodic reactions

Mechanism Of Electrochemical Corrosion

Anodic Reaction:

Dissolution of metal takes place.

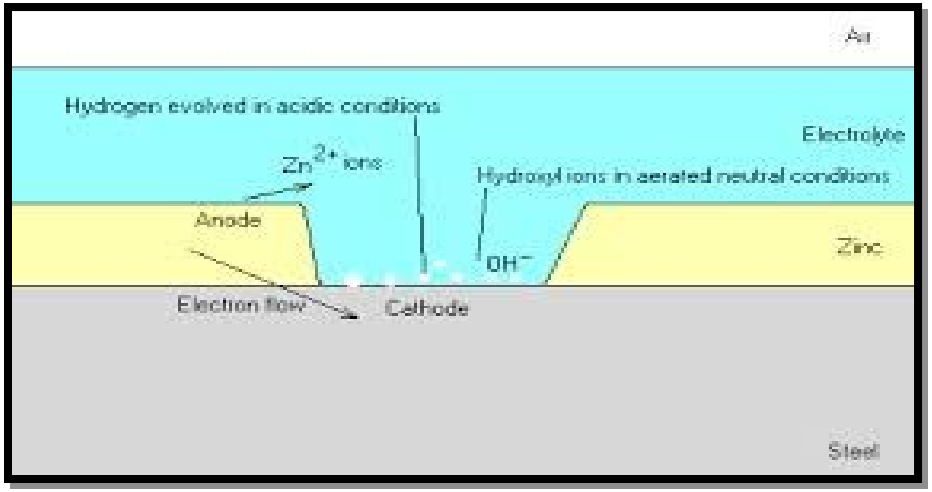
As result metal ions are formed with the liberation of free electrons.

$$M \leftrightarrow \underset{\text{Metal Ion}}{M^{+n}} + e^-$$

Cathodic Reaction

(i) Hydrogen Evolution :- Occurs usually in acidic medium

$$2H^{+} + 2e^{-} \leftrightarrow H_2\ (g)$$



(ii) Oxygen Absorption :- occurs when solution is aerated sufficiently.

$$O_2 + 4H^{+} + 4e^{-} \leftrightarrow 2H_2O \quad \text{(In acidic medium)}$$

$$O_2 + 4H^{+} + 4e^{-} \leftrightarrow 4OH^{-} \quad \text{(In basic medium)}$$

Wet corrosion takes by the following ways.

- Hydrogen gas evolution
- Oxygen gas absorption

This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

Anode: Fe----→ $Fe_2^+ + 2e^-$ (Oxidation)

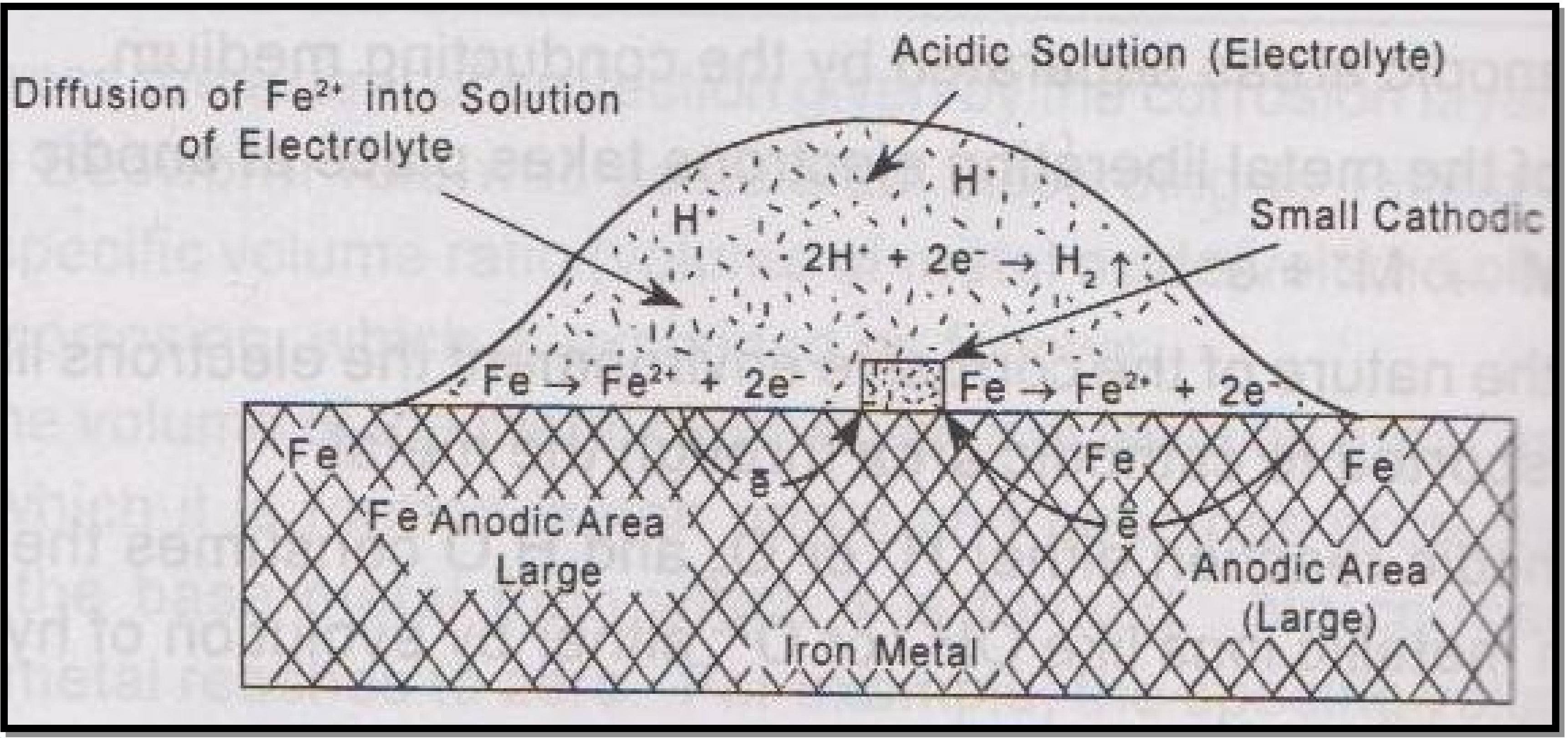
- The electrons released flow through the metal from anode to cathode, whereas H+ ions of acidic solution are eliminated as hydrogen gas.

Cathode: $2H^+ + 2e^-$ ----→H_2 (Reduction)

- The overall reaction is: $Fe + 2H^+$ -----→$Fe_2^+ + H_2$

- All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas.

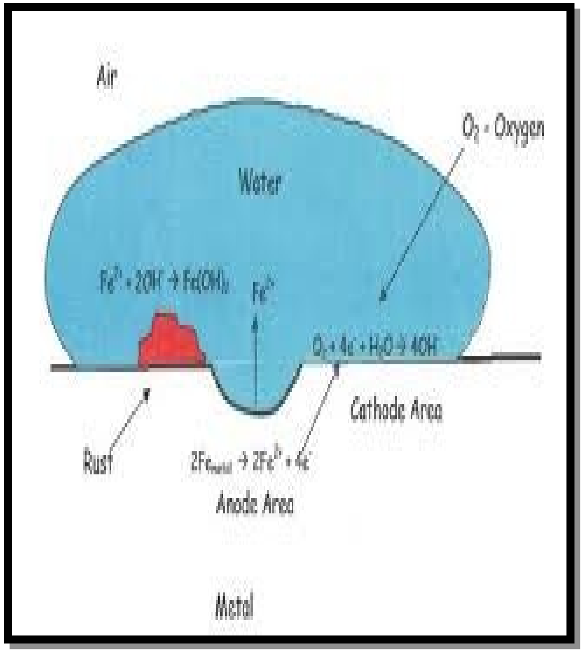
Mechanism of wet corrosion by hydrogen evolution



Absorption of oxygen

Absorption of oxygen: For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen.

- Usually the surface of iron is coated with a thin film of iron oxide.
- If the film develops cracks, anodic areas are created on the surface.
- While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.

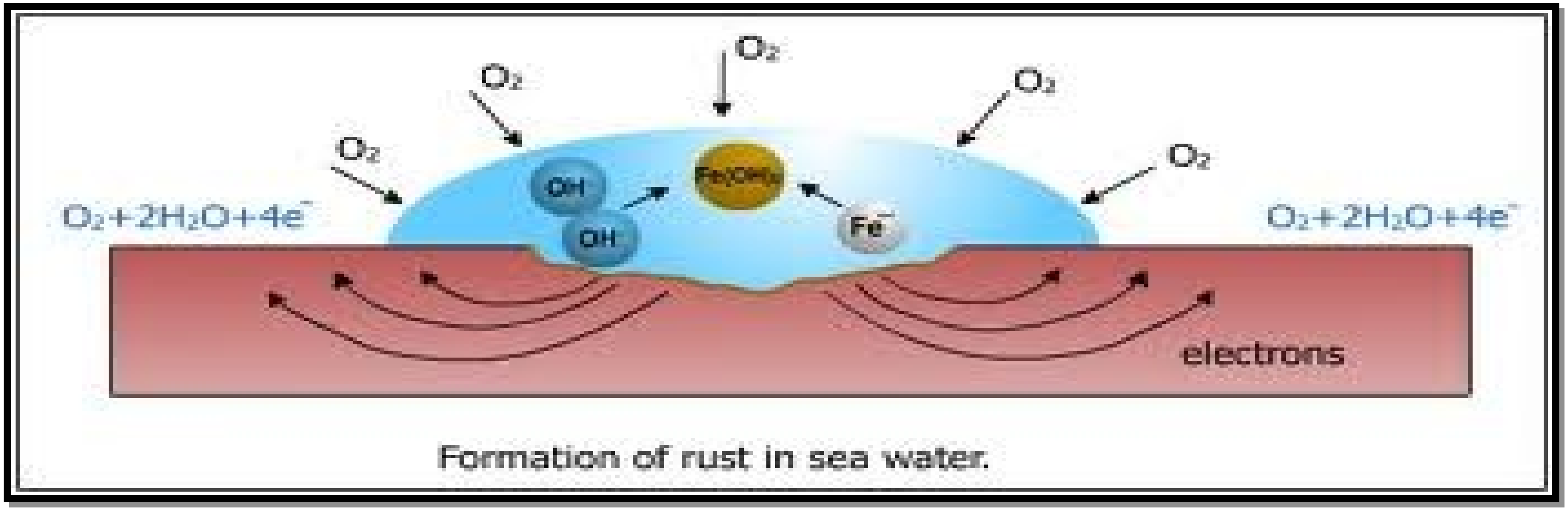


The released electrons flow from anode to cathode through iron metal.

.

At anode: Fe ----→$Fe_2^+ + 2e^-$ (Oxidation)
At cathode: ½ $O_2 + H_2O + 2e^-$ ---→$2OH^-$ (Reduction)
Overall reaction: $Fe_2^+ + 2OH^-$ -----→ $Fe(OH)_2$

The product called yellow rust corresponds to $Fe_2O_3 . 3H_2O$



Formation of rust in sea water.

FACTORS EFFECTING THE CORROSION

- The factors that effect corrosion are

  i) Nature of the metal

  ii) Nature of the environment

Nature of the metal

- The rate and the extent of corrosion depends on the following factors

A) Purity of a metal
B) Position in galvanic series
C) Over voltage
D) Nature of oxide film
E) Nature of corrosion product

Nature of the metal

1. ***Purity of the metal***: Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.

2.***Electrode potentials:*** metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (e.g.. Zn, Mg, Al etc.).

3.Position of metal in Galvanic series: Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.

The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.

***4.Relative areas of anodic and cathodic cells**:* When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. *i.e,* the relative areas o of corrosion is influenced by cathodic to anodic cells.

5. ***Physical state of metal**:* Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

6. ***Hydrogen over voltage:*** when a cathode reaction is hydrogen evolution type, the metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, since the liberation of hydrogen gas is easy at this condition. Hence the cathodic reaction is very fast which in turn makes anodic reaction fast. Hence the rate of corrosion increases. Higher the over voltage, lesser is the corrosion.

7. ***Nature of surface film****:* If the corrosion product formed is more stable, insoluble and non porous, it acts as protective layer and prevents further corrosion (E.g.. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

Nature of the environment

1. Temperature: the rate of corrosion reactions increases with increase in temperature.

2. Humidity in air: the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.

3. Presence of impurities: Atmosphere is contaminated with gases like CO_2, SO_2, H_2S; fumes of H_2SO_4, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion.

4. pH value: pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.

5. Amount of oxygen in atmosphere**:** As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

6.Velocity of ions which flow in the medium: As the velocity of the diffusion of the ions in the medium increases, the rate of corrosion increases .

CORROSION CONTROL METHODS

The various measures taken for corrosion protection are

I) CATHODIC PROTECTION

II) SURFACE COATINGS

CATHODIC PROTECTION

- The method of protecting metals and alloys from corrosion making them completely cathode.

- To achieve this auxilary anode is provided in the corroding medium which is connected to the structure.

- Cathodic protection is of two types

i) Sacrificial anodic method

ii) Impressed current cathodic method

Cathodic Protection

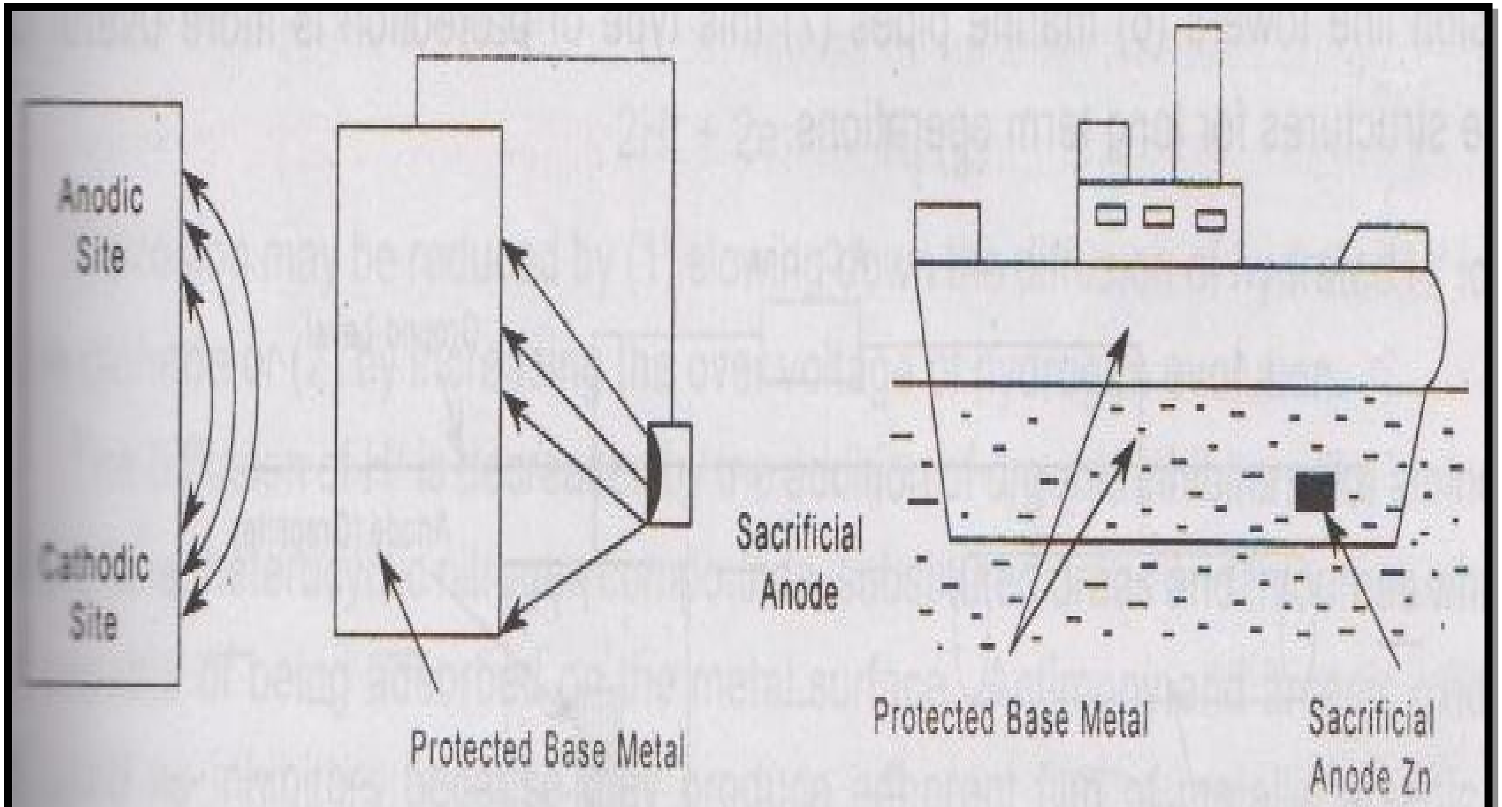
Force the metal to be protected to behave like cathode.

(i) **Sacrificial anodic protection**:

- Metal to be protected from corrosion connected to more anodic metal
- Commonly used metals Mg, Zn, Al and their alloys

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



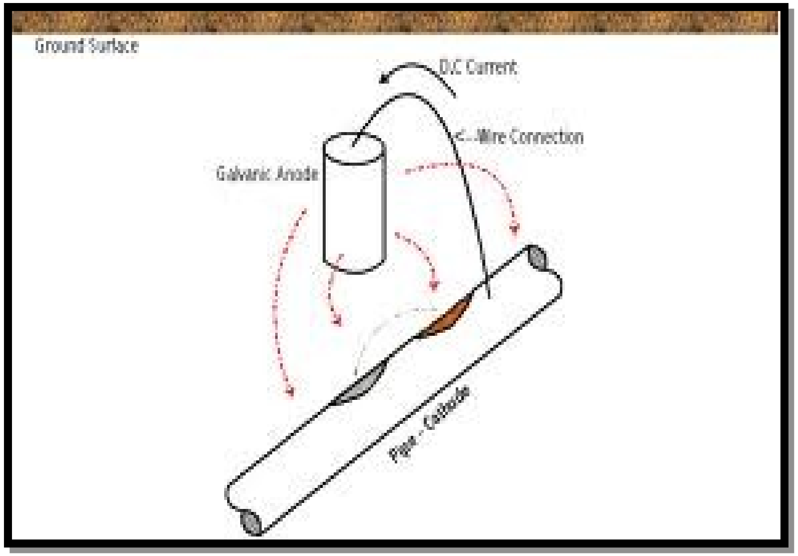
Unprotected metal being corroded

(b) Sacrificial anodic protection

(c) Protection of ship-hull below water line by

Impressed current method:

- Direct current is applied in opposite direction to nullify the corrosion current
- Converts the corroding metal from anode to cathode.



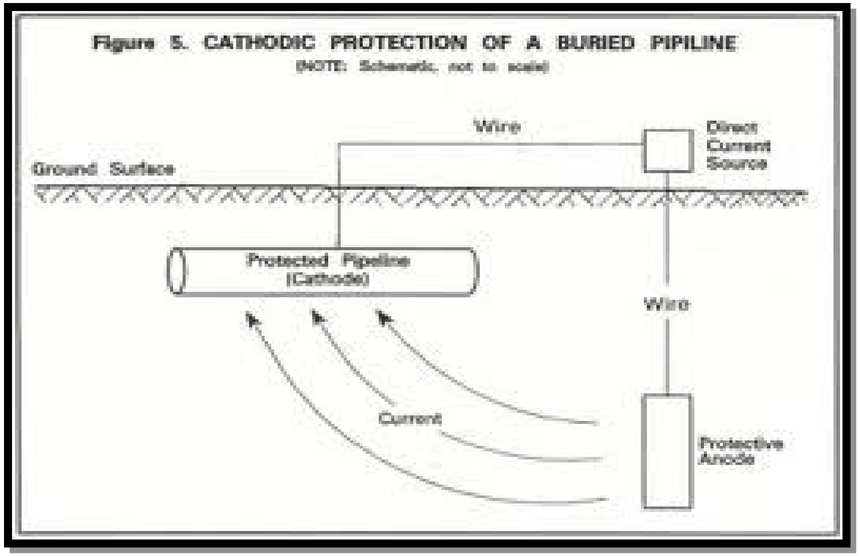
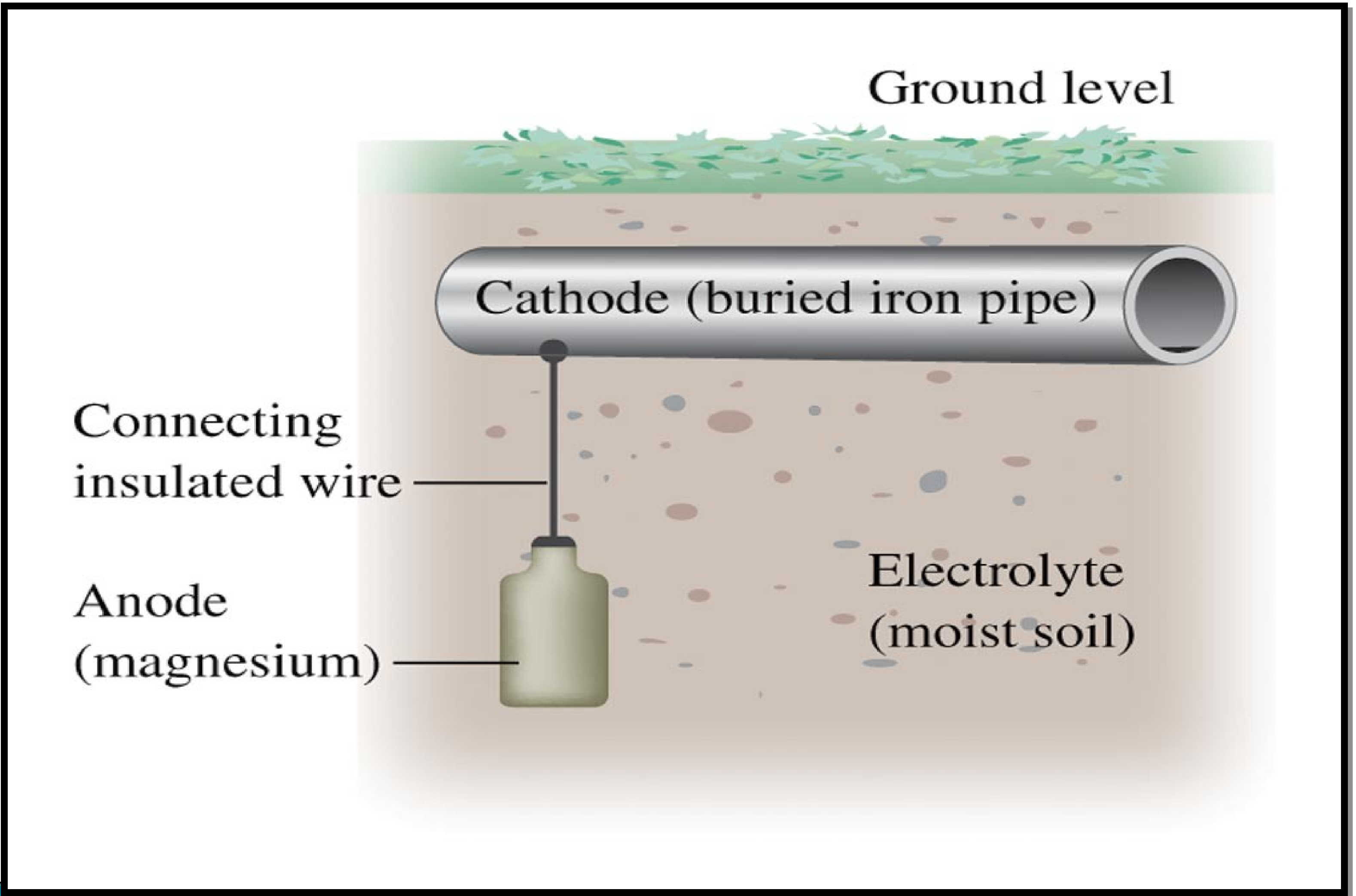


Figure 5. CATHODIC PROTECTION OF A BURIED PIPILINE
(NOTE: Schematic, not to scale)


Ground level
Cathode (buried iron pipe)
Connecting insulated wire
Anode (magnesium)
Electrolyte (moist soil)

SURFACE COATINGS

- The metal surface is covered with a coating to protect it from corrosion.
- These may be

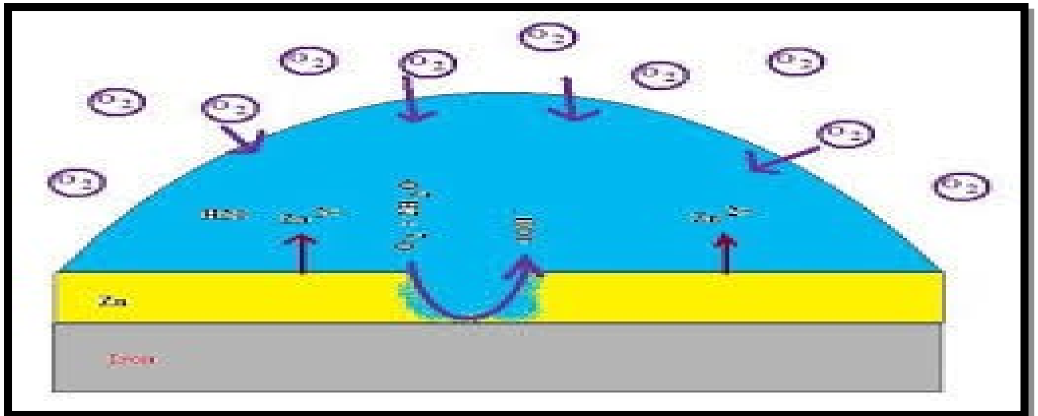
    i) Metallic

    ii) Organic

METALLIC COATINGS

The metals used for coatings may be placed under two categories

i) metals which are anodic to the metal i.e., metals above it in galvanic series.



ii) metals which are cathodic to the metal i.e., metals below it in galvanic series.

Methods of applications of metal coatings:

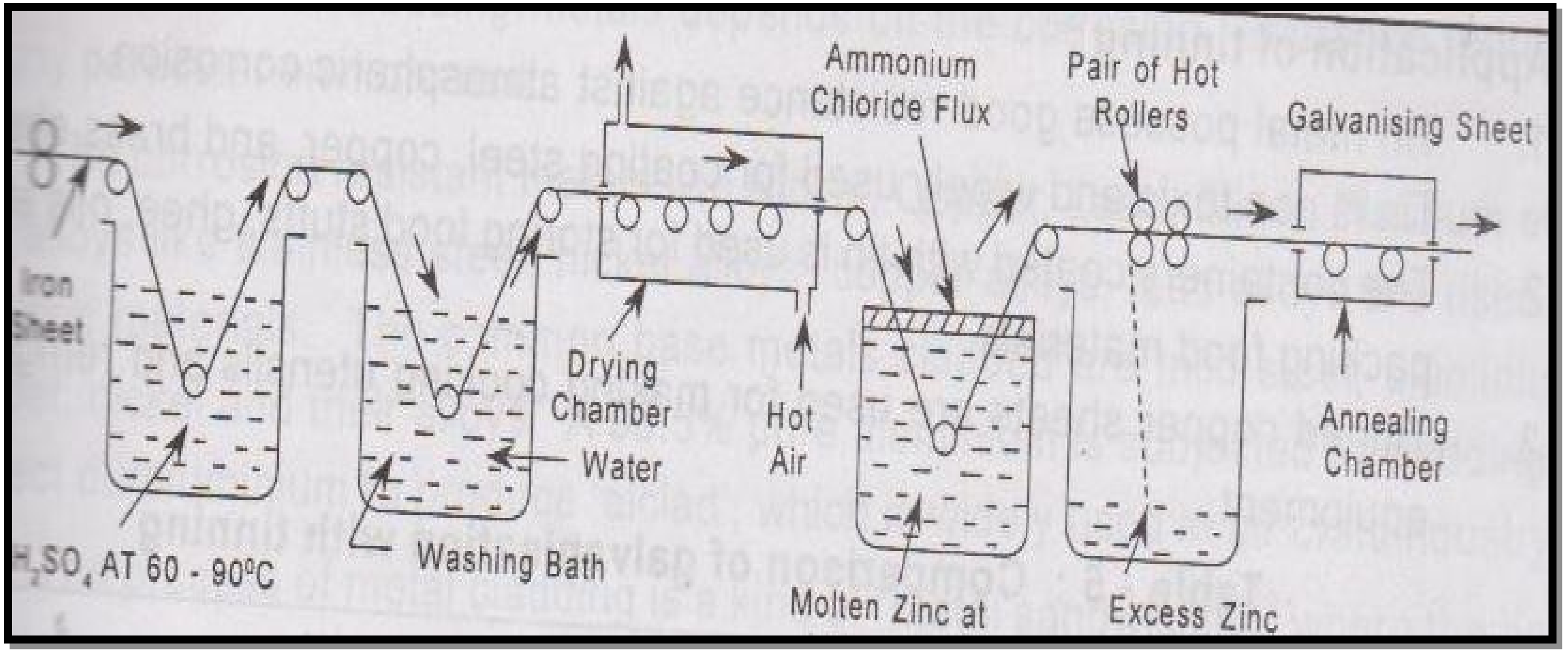
- Hot dipping: This technique is most widely used to control corrosion. Hot dipping is used for producing a coating for low melting metals such as Zn, Sn, pb ,Al.
- on Iron, steel, copper which are having high melting point usually underwent into corrosion due to their oxidising property.
- The process in general consisting of immersed a metal in a bath of its molten coating& covered by a molten layer.
- The flux cleans the base metal& prevent oxidation of metal coating with molten solution.

- Hot dipping is widely applied either by
  (1)GALVANIZING (2)TINNING

Galvanizing

- It is the process in which iron or steel is protected from corrosion by coating with a thin layer of zinc.
- Iron or steel is first cleaned by pickling with dil. H_2SO_4 solution for 15-20 mts at 60^0-90^0c. The steel is then washed well and dried .
- Then the metal sheet is dipped in bath of molten Zinc maintained at 425^0-430^0c. The surface of bath is kept covered with a $Zncl_2$ flux to prevent oxide formation.
- Then the metal sheet is passed through a pair of hot rollers which removes excess of Zinc and maintain uniform thickness of Zinc on metal sheet.

- The sheet is subjected to annealing process at 65^0c and cooled slowly.



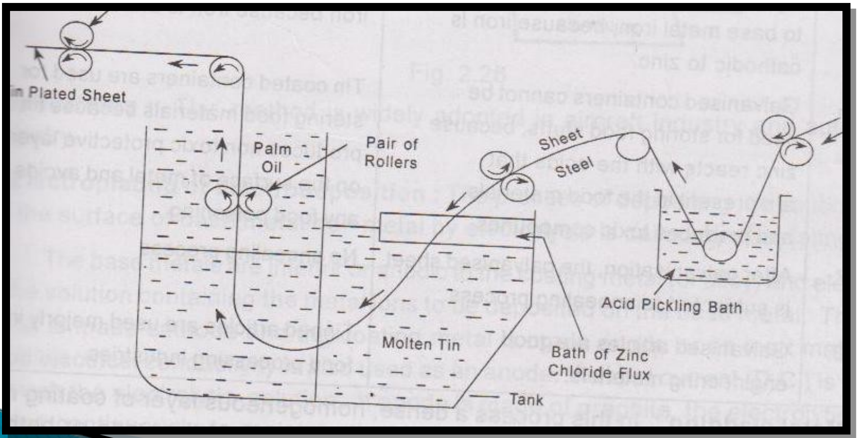
Uses of Galvanization: It is used to protect Iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets, and tubes.

Defects :Galvanised utensils are not used for cooking because of solubility of Zn.

TINNING

- Tinning is the process of coating of tin over the Iron sheet or steel articles
- A cleaned iron sheet is passed through a bath of molten flux, then passes through a tank of molten tin and finally through a layer of palm oil which protect hot tin coated surface against oxidation.

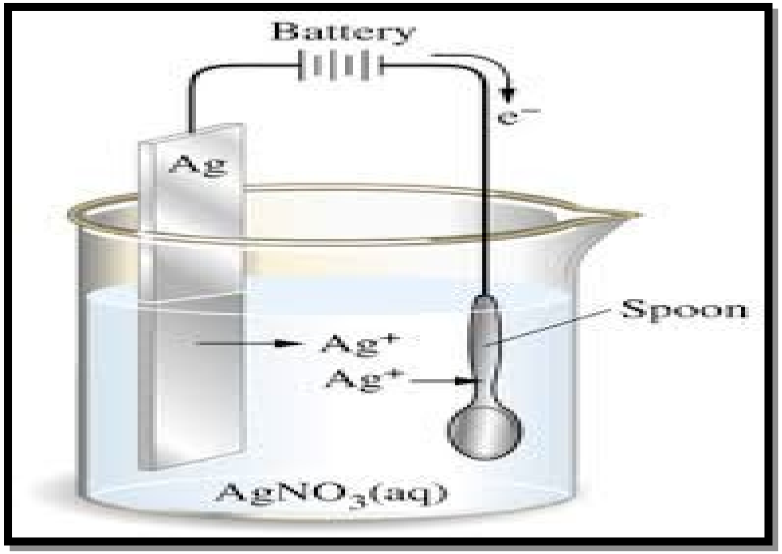
Uses: (1)It is widely used for coating of steel, copper, brass & bronze etc . It is used to store food stuff, ghee oils, kerosene& pickels and used for refrigerators equipment.



ELECTROPLATING

- Deposition of coating metal on the base metal by passing direct current through an electrolytic solution which contain the soluble salts of the coating material.
- Pure metal is made as cathode and base metal as anode.
- Electrochemically coat metal is deposited on base metal.
- This metal gives smooth, fine and uniform coating
- It depends on

(i) Temperature



(ii) Current density

(iii) Electrolyte Concentration

(iv)Nature of base met (v) Time

Applications of Electroplating

- It is most important & frequently used technique in industries to produce metallic coating

- Both metals & non metals can be electroplated.

- In metals the electroplating increases resistance to corrosion, chemical attack, hardness, wear resistance and surface properties.

- In non metals electroplating increases strength and decorates the surface of non metal like plastics, wood, glass.

Electroless Ni plating:

- Pre treatment of surface:
- (1) CO, Ni, steel and Al can be directly plated.
- (2)Pb, Cd and Sn are first electroplated with Ni prior to electroless plating.
- (3)Non conductors are activated in Sncl$_2$ & HCl followed by dipping in Pdcl$_2$,Hcl.on drying thin pd layer is formed.

Organic paints

ORGANIC COATINGS

- Organic coatings protect the surface as they act as physical barriers between the metal to be protected and the corroding environment and are decorative.

- The extent of protection given by the organic coatings depends on

  A) Impermeability to gases ,salts and water

  B) Chemical inertness to the corrosive environment

  C) Good surface adhesion

The Organic & Natural paint co.

PAINTS

- Paints form a protective layer over the surface of the metal to prevent corrosion.

The main constituents of the paints are

- Pigment
- Vehicle
- Thinner
- Driers
- Fillers
- Plasticizers
- Anti skinning agents

Pigment

- It is a solid constituent that obscures the surface and provides a decorative color.
- A liquid binds the pigment to the surface and protects it from decay.
- It usually comprises of 60 to 80% of the weight of the paint film.
- Increases the life of paint film since it prevents the entry of ultra violet rays.
- E.g.; lead oxide, red lead, lead chromate etc.,

Vehicle

- Film forming constituent of the paint.
- They hold the pigment on the metal surface.
- They give metal adhesion to the metal surface.
- They impart durability and toughness to the film.
- They isomerize , polymerize and condense to form characteristic tough, elastic ,coherent, highly cross linked structured macromolecular film.
- E.g.: mustard and sunflower oil etc.,

Thinners

- Viscosity is reduced by the addition of thinners.
- It is a volatile solvent helps to adjust the consistency of the paint.
- Thinner being volatile evaporates.
- They remain permanently in paints and varnishes.
- They improve elasticity of the film.
- They suspend the pigments in the paints.

E.g. Turpentine, mineral spirits, xylol, kerosene.

Fillers

- They are inert materials.
- They are used to improve the properties of the paints.
- They reduce the cost of paints.
- They serve to fill the voids in the film.
- Increases the random arrangement of pigment particles.
- Improves the durability of the film.
- E.g.: talc, chalk, silica etc.,

Driers

- Drying of the oil film is accelerated or catalyzed by driers.
- To reduce the drying time a drier is added.
- They are oxygen carrier catalyst.
- To improve the drying quality of oil film.
- This is done by condensation , oxidation and polymerization.

E.g. linoleates , borates, resinates etc.,

Plasticizers & Anti skinning agents

- They remain permanently in paints and varnishes.
- They improve elasticity of the film.
- To prevent cracking of the film.
- Anti skinning agents prevent the gelling and skinning of the paint film.

E.g.: tricresyl phosphate, tri phenyl phosphate,
di butyl tartarate etc.,


Thank
You

UNIT III

POLYMERIC MATERIALS

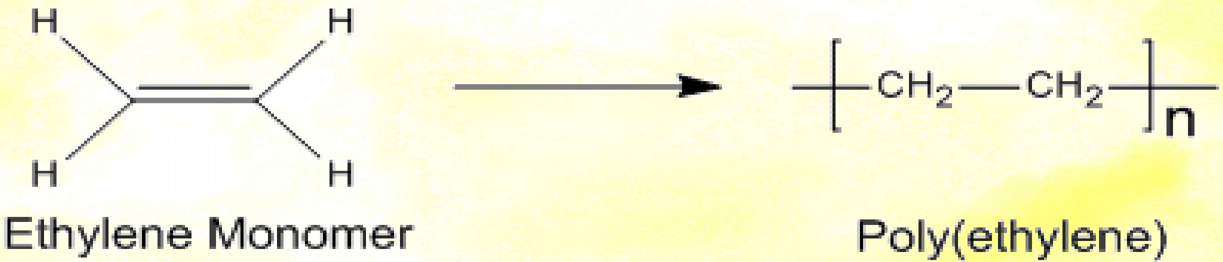
POLYMER

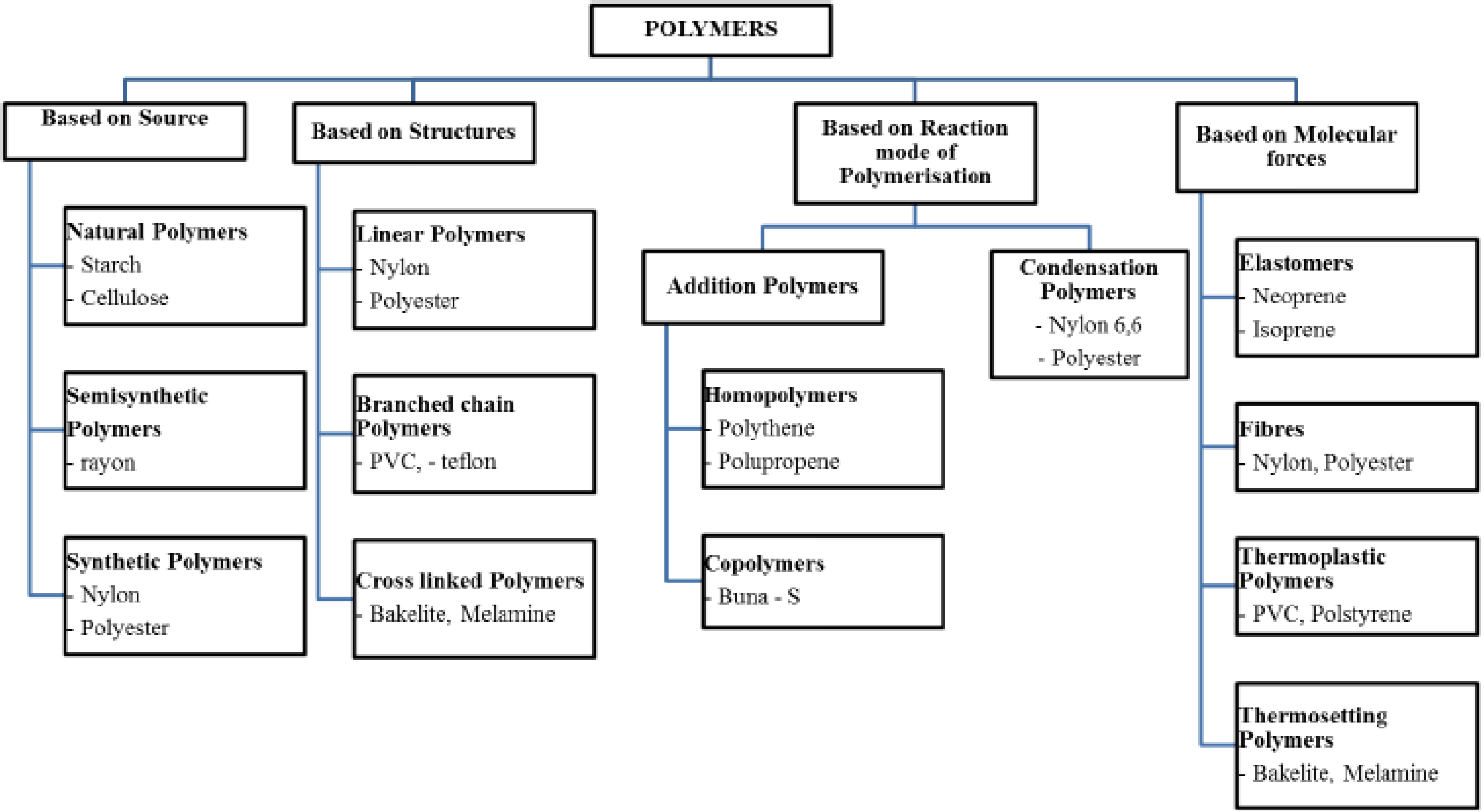
A word polymer is a combination of two greek words, “poly” means many and “mer” means parts of units.

DEFINITION: Polymers are macromolecules which are formed by linking together of a large number of small molecules called monomers.

Example: polythene is a polymer formed by linking together of a large number of ethene molecules.

Polymerisation: A process of forming polymer is called polymerisation.





POLYMERS

- **Based on Source**
  - **Natural Polymers**
    - Starch
    - Cellulose
  - **Semisynthetic Polymers**
    - rayon
  - **Synthetic Polymers**
    - Nylon
    - Polyester
- **Based on Structures**
  - **Linear Polymers**
    - Nylon
    - Polyester
  - **Branched chain Polymers**
    - PVC, - teflon
  - **Cross linked Polymers**
    - Bakelite, Melamine
- **Based on Reaction mode of Polymerisation**
  - **Addition Polymers**
    - **Homopolymers**
      - Polythene
      - Polupropene
    - **Copolymers**
      - Buna - S
  - **Condensation Polymers**
    - Nylon 6,6
    - Polyester
- **Based on Molecular forces**
  - **Elastomers**
    - Neoprene
    - Isoprene
  - **Fibres**
    - Nylon, Polyester
  - **Thermoplastic Polymers**
    - PVC, Polstyrene
  - **Thermosetting Polymers**
    - Bakelite, Melamine

Classification of polymers

Polymers can be classified in a number of ways.

Classification based on the source:
Natural polymers: Which are found in nature in animals and plants.. For example starch, cellulose, proteins, natural rubber etc.

Synthetic polymers: Man made polymers are known as synthetic polymer. eg. PVC, polyethylene, polystyrene, nylon-6, nylon-6,6; nylon-6,10; terylene, synthetic rubbers etc.

Classification based upon structure:
Linear polymers: Monomers are joined together to form long straight chains. The various linear polymeric chains are stacked over one another to give a well packed structure close packed in nature, having high densities, high melting point and high tensile (pulling) strength.
Example: polythene, nylons, polyester, etc.

Branched chain polymers: Polymers in which the monomeric units constitute a branched chain. Branched chain polymers have lower melting point low densities and tensile strength as compared to linear polymers.
Examples are amylopectin, glycogen, low density polyethylene and all vulcanized rubbers

Cross linked or Three-Dimensional network polymers:

When linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross linked polymers are always condensation polymers.
Examples: Bakelite urea-formaldehyde, etc.

Classification based upon molecular force:

Elastomers: Polymers in which the intermolecular forces of attraction between the polymer chains are the weakest (weak van der Waals forces of attraction) these polymers consist of randomly coiled molecular chains of irregular shape having a few cross links.
Examples are natural rubber, Buna-S, Buna-N etc.

Fibers: Those polymers in which the intermolecular forces of attraction are the strongest are called fibers. These polymers held together by H-bonding or dipole-dipole interaction. Fibres have high tensile strength, least elasticity having high melting point and low solubility.
Examples: Nylon 6:6, polyester, rayon, etc.

Thermoplastics: In thermoplastics intermolecular forces of attraction are in between those of elastomers and fibres. Thermoplastics become soft and viscous on heating and rigid on cooling. Examples are polythene, nylon-6, nylon-6:6, etc.

Thermosetting polymers: These polymers have low molecular masses and are semi-fluid substances. These polymers are hard and infusible.
Examples are melamine-formaldehyde, bakelite (phenol-formaldehyde) etc.

Classification based upon polymerisation:

Addition polymerization: A polymer formed by direct addition of repeated monomer possessing double or triple bond, without elimination of small molecule is called addition polymerisation.
Examples: polythene, PVC, etc.

Condensation polymerisation: A polymer formed by a reaction occurring between monomers containing polar groups, with the elimination of small groups like water, HCl, ammonia, etc. is called condensation polymerisation.
Examples: Nylon 6:6, terylene

Classification based upon monomers:

Homopolymers: If a polymer consists of one kind of monomers then it is called a homopolymer.
Examples: polythene, teflon, PVC, etc.

Copolymer: If a polymer consists of more than one kind of monomers is called a copolymer.
Examples: Nylon 6:6, polyester, Bakelite, Buna-S, etc.

Plastics/ Plastic Material

Definition: Organic materials which can be moulded into any desired form, when subjected to heat and pressure in presence of a catalyst.

Terms resin and plastics are now-a-day considered synonyms. However, both are different.

Resins: are the basic binding material which form a major part of th plastics and which has undergone polymerisation reaction during preparation.

Unique properties of plastics

- Lightness in weight
- Good thermal and electrical insulation
- Corrosion resistance
- Easy workability
- Adhesiveness
- Low fabrication cost
- Decorative surface effect
- Easy moulding
- Insect resistant
- Capable to being made to order
- Absorbent of vibrations and sound

- Low thermal expansion coefficient
- Chemical inertness
- Transparency
- Low maintenance cost
- Low softening points
- Ability to take variety of colours, shades, etc.
- Good shock absorption capacity
- High resistance to abrasion
- Impermeable to water
- Good strength and toughness
- Excellent in finish

Uses of Plastics

- Making electrical goods and appliances
- Aeronautical engineering
- Making furniture
- Making floor and wall linings
- Making special types of paints
- Heat and sound insulation
- Making windscreens, laminated glasses, table tops
- Preparing decorative laminates and mouldings

- Making overhead tanks, water pipes
- Making household articles
- Making synthetic fibres
- Making adhesives
- As water softening agents
- Making films for waterproofing, damp proofing and curing of concrete

Preparation of plastics

Prepared using- Polymerisation reaction it is of 2 types:

1. Addition Polymerisation: involves repeated addition of monomers to yield long chains of polymer.
2. Condensation Polymerisation: involves condensation/combination of 2 monomers resulting in loss of small molecules like H_2O, HCl, NH_3 etc. to yield a polymer.

POLY VINYL CHLORIDE (PVC)

Properties of PVC:

- Colourless
- Odourless
- Chemically inert,
- resistant to light, atmospheric oxygen,
- Acids and alkalis
- Pure resin possesses high softening point(148 ^{o}C)
- Greater stiffness, high rigidity
- It is brittle

Engineering applications of PVC

Unplasticized PVC

Used for making sheets employed for

- tank-linings

- light fittings
- safety helmets
- refrigerated components
- tyres
- cycle and motorcycle mudguards

Plasticized PVC(adding plasticizers)

Used for making sheets employed

- Rain coats

- Table cloths
- Curtains
- Covering of electrical cables
- Toys, tool handles, toiled good
- Plastic coated cloth
- Thermal insulating foam

TEFLON (Poly Tetra Fluoro Ethane)

Properties of Teflon:

- Extreme tough
- High softening point(350 ◦C)
- High chemical resistance to chemicals(except hot alkali metal and hot fluorine)
- Waxy touch, very low coefficient of friction
- Good electrical & mechanical properties
- It can be machined, punched & drilled

Engineering Applications of Teflon

Used for:

- Insulating material(motors, transformers,cables, wires, fittings etc)
- For making gaskets, packings, pump parts, tank linings, chemical carrying pipes, tanks, tubings
- For coating & impregnating glass fibres, cloths
- In non lubricating bearings
- Non sticking stopcocks for burettes

BAKELITE

Properties of Bakelite:

- Hard
- Rigid
- Scratch resistant
- Infusible
- Water resistant
- Resistant to acids, salts, organic solvents
- Attacked by alkalis
- Excellent electrical insulator

Engineering Applications of Bakelite

Used for making

<u>Electrical insulator parts like</u>

- Switches
- Plugs
- Switch boards
- Heater Handles

<u>Moulded articles like</u>

- Telephone parts
- Cabinets for radio and television

Also used in:

- Paints and varnishes
- As adhesives(binder) for grinding wheels
- As ion-exchange resins in water softening
- For making bearings, used in propeller shafts for paper industry and rolling mills

FIBRES

- Fibres are thread like structures that are thin, long and flexible strands

- There are two types of fibres:

1) Natural fibre- obtained from natural sources
   Examples- Silk, cotton,wool, jute etc

2) Synthetic fibre- Which are man made
   Examples- Rayon, Nylon, acrylic etc

Properties of Nylon Fibres

- Translucent
- Whitish, horn
- High melting point(160-264 °C)
- High tensile strength
- High temperature stability
- High abrasion resistance
- Insoluble in organic solvents
- Soluble in phenol and formic acid
- Have good strength

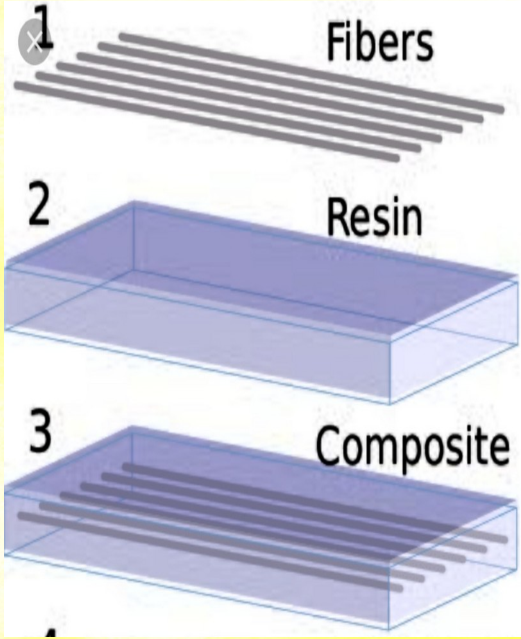
- Light, high melting
- Absorb little moisture(drip-dry in nature)
- Very flexible
- Regain original shape after use
- Resistant to abrasion
- On blending with wool, the strength & abrasion resistance increases
- Good physical strength and self lubricating properties

Engineering applications of Nylon

Used as:

- Thread in bristles for toothbrushes
- As gears, fittings & bearings, automotive industry
- Threads, ropes, filaments, nets
- Gun frames
- Surgical sutures
- Strings for musical instruments
- In hosiery and knitted garments
- Used to make ropes for rock climbing & parachutes

Fibre-reinforced plastic(FRP)



It is a composite material made of a polymer matrix reinforced with fibres

Fibres- They provide strength & stiffness.

- Common fibres used are glass, carbon, aramid, basalt
- Other fibres are paper, wood, asbestos

Matrix- Protects & transfers load between fibres & also supports them under compression loading.

- Common matrices are epoxy, vinyl ester, polyester, Polylactide etc.
- The original plastic without fibre reinforcement is known as matrix or binding agent

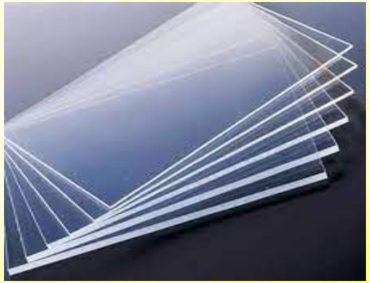
Properties of FRPs

- Light weight
- Corrosion resistance
- High tensile strength
- Non magnetic properties
- Specific stiffness
- High specific strength
- Easily constructed
- Ease of handling
- UV radiation stability
- Resistant to chemicals

Examples of FRPs

- GFRP (Glass Fiber Reinforced Polymer)
- CFRP (Carbon Fiber Reinforced Polymer)
- AFRP (Aramid Fiber Reinforced Polymer)

Glass Fibre Reinforced Plastic (GFRP):



- Commonly known as fiberglass
- Is synthetic material made by plastic (forms matrix) & extremely fine fibres of a glass.
    - Fibre: Glass fibre (E- glass, S- glass, R- glass)
    - Matrix: poly ester, epoxy, vinyl ester, poly styrene, polycarbonate etc.
- Glass fibres are made by mixing sand, limestone, folic acid and the mixture is heated about 1260 °C

Glass Fibre Reinforced Plastic (GFRP):

Advantages:

- High tensile strength
- light weight, strong, less brittle
- Heat resistant, weather resistant, insect resistant
- Corrosion resistant, chemical resistant (except HF, H_3PO_4)
- Dimensional stability: will not stretch or shrink
- Low moisture absorption
- Good electrical insulator
- Easy processing: ability to get molded into various complex shapes
- Incombustibility: doesn't support flame or emit smoke or toxic waste when exposed to heat

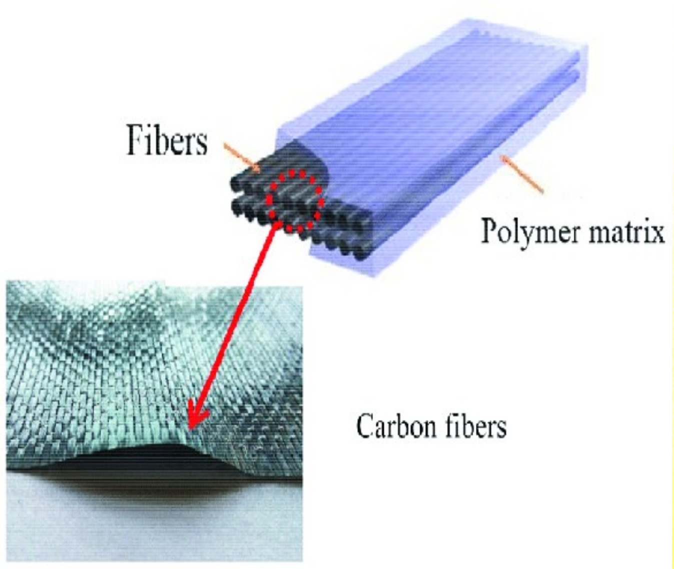
Applications:

- Manufacturing of automotive bodies: due to its lightweight
- Roofs, domes, pipes
- Boats
- Aquariums, fountains, waterslides, hot tubs, bath tubs, Surf boards, Gliders : due to anti-slip property
- Pump castings
- Storage containers
- for electromagnetic windows
- Screening for cooling towers
- Making aviation equipment and ducts (engine cowlings, bulkheads, storage bins and ground handling equipment)


APPLICATION
YD
SURF BOARD
COMPOUND MATERIAL
WELDING
HEAT PRESERVATION

Carbon Fiber Reinforced Polymer

- CFRP the reinforcement material is carbon fibre
- <u>Carbon fibre:</u> is a long thin strand of carbon atoms which are bonded together in microscopic crystals that are woven together into a fabric
- Carbon fibers are microscopically small and about eight times thinner than a human hair.
- Carbon fibre can be combined with matrix to make almost any shape.
- <u>Matrix:</u> polymer resin such as epoxy, polyester, vinyl ester, nylon
- CFRP is five times lighter than steel and has only about 60% of the weight of aluminium.
- Thus CFRP's replaces steel and aluminium in a variety of industries.



Carbon Fiber Reinforced Polymers

Properties:

- Extremely strong
- Light weight
- High tensile strength
- High chemical inertness
- Good corrosion resistance
- Low thermal expansion
- X- ray transparency
- Low density
- Vibration resistance
- Low thermal conductivity
- Good rigidity
- Non magnetic
- Bad conductor of electricity

Applications:

Used in manufacturing of

Automotive field:

- Racing car bodies
- Vehicle parts such as body components

Marine field: Boats, submarines, yacht

Spacecraft & aerospace :

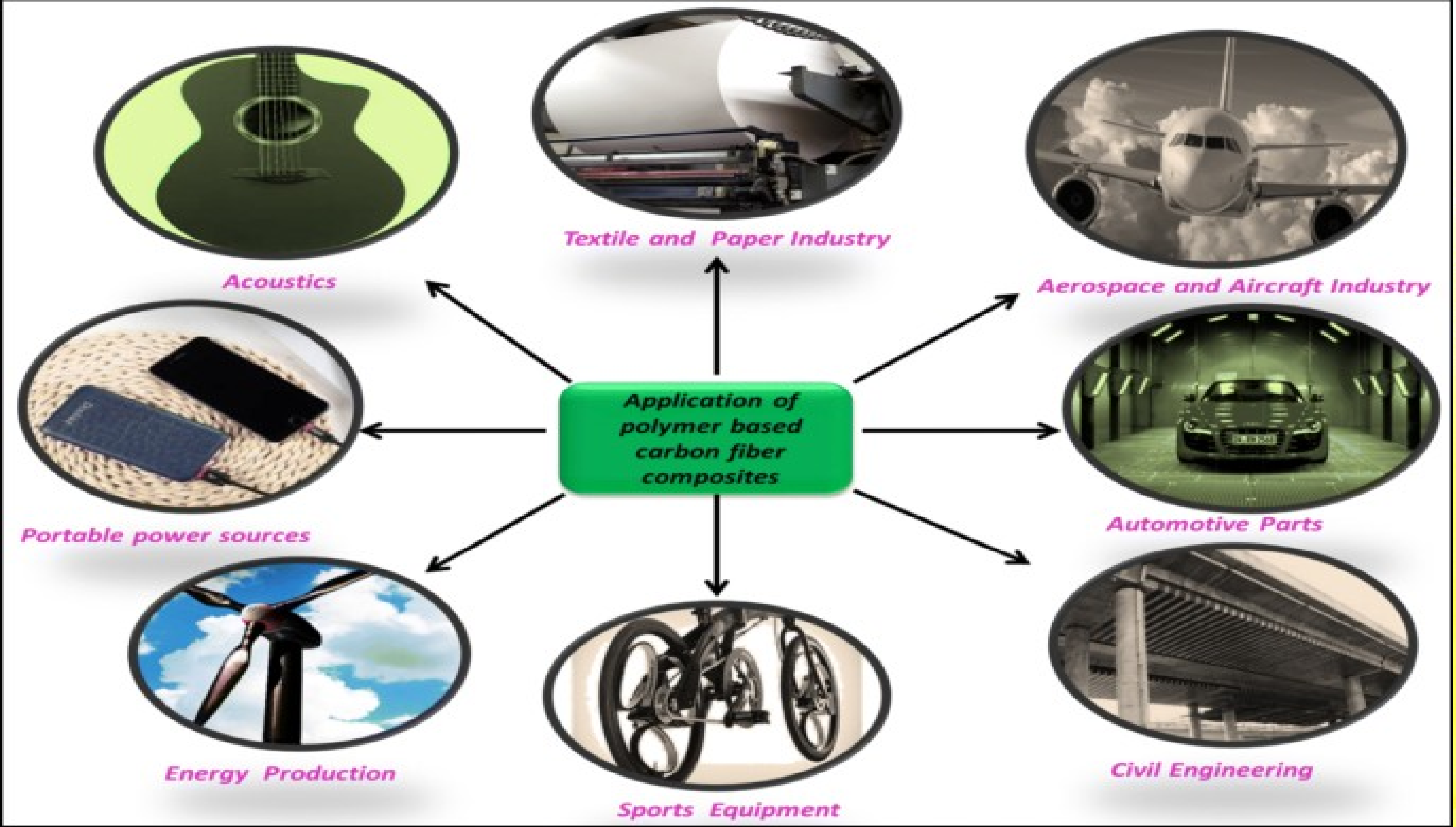
- Main body of the plane, parts of the wings & tail parts

Sports goods:

- Golf club shafts
- Tennis racquets

Others:

- Fishing rods
- Bicycle frames
- Racing car bodies
- Robotic arms


Application of polymer based carbon fiber composites
Acoustics
Textile and Paper Industry
Aerospace and Aircraft Industry
Portable power sources
Automotive Parts
Energy Production
Sports Equipment
Civil Engineering

Aramid fibres

In AFRP the reinforcement material is aramid fibre

Aramid fibres are high strength fibres which are made by aromatic polyamide

Matrix: epoxy, polyester, vinyl ester

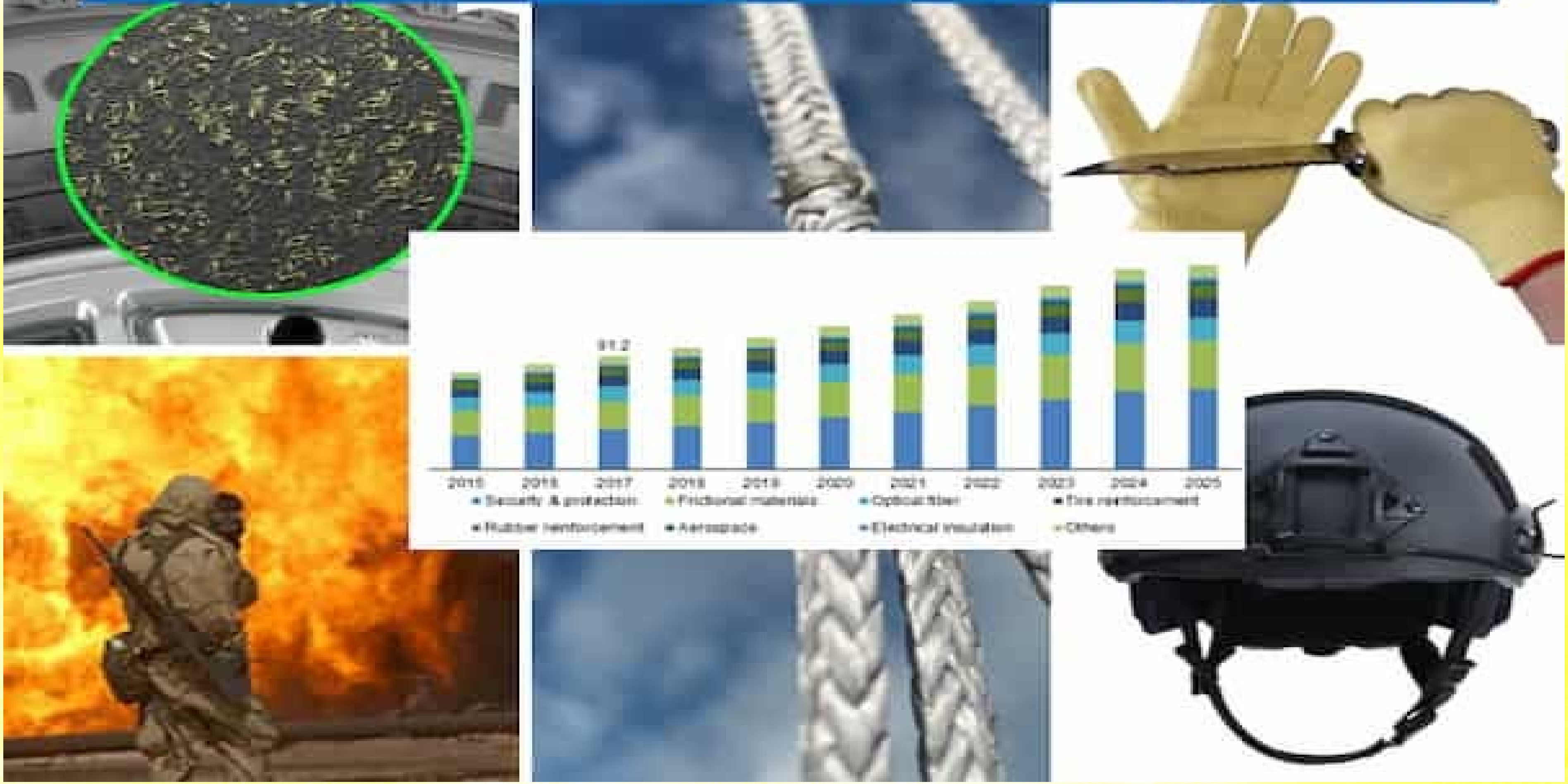
Properties:

- High tensile strength
- Flame resistance
- High chemical resistance
- High compression strength
- High elasticity
- High abrasion resistance
- Low weight

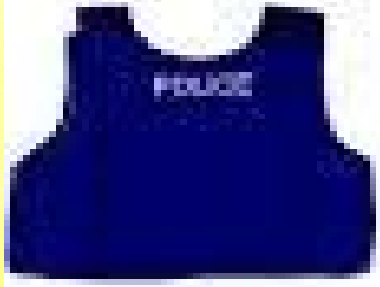
Applications:

- Bullet proof vests
- Fire protection cloths
- Protective gloves, helmets, body armor
- Sports goods
- Aircraft & military vehicles
- Ropes and cables

Aramid- The Ideal Shield for Defence Applications



BULLET / STAB
PROOF VESTS



DIVING GLOVES

WALKING BOOTS

MILITARY HELMET

CUT RESISTANT
GLOVES

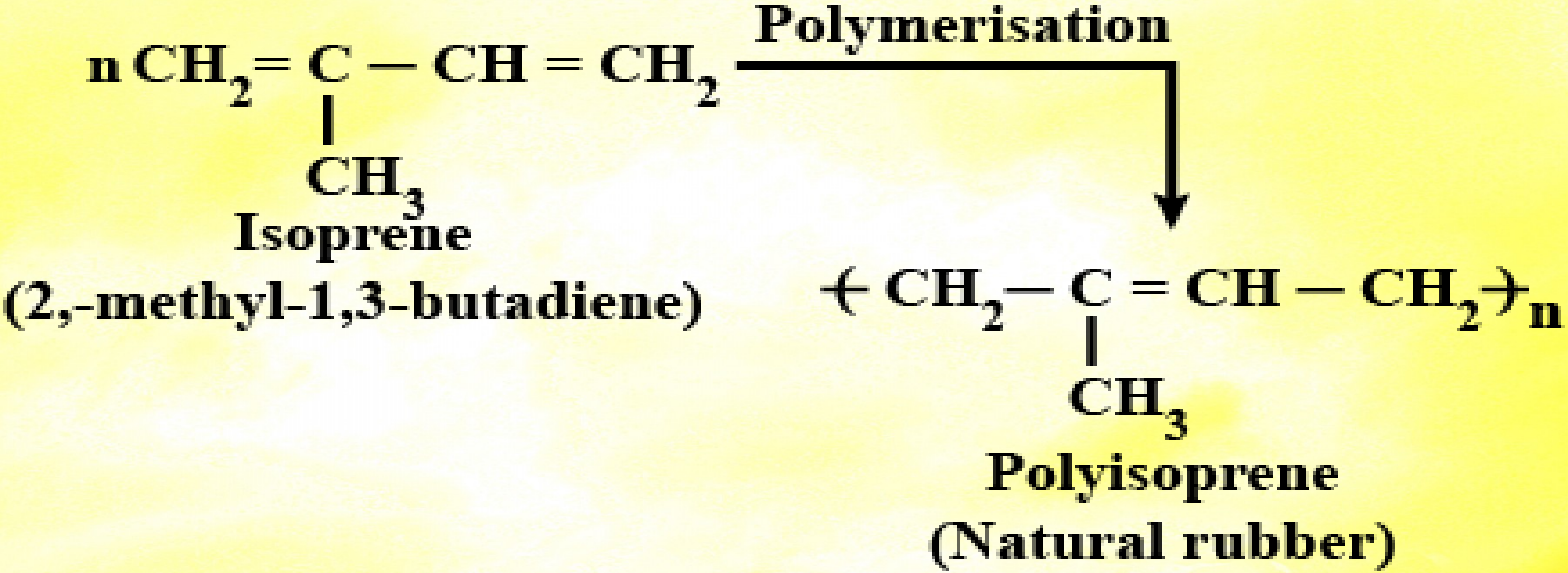
BICYCLE TYRES

CAR TYRES

FIRE PROOF
CLOTHING

Natural Rubber

Natural rubber is a natural polymer of organic compound isoprene obtained from the bark of the rubber trees.



$$n\,CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerisation}} \left(CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2\right)_n$$

Isoprene
(2,-methyl-1,3-butadiene)

Polyisoprene
(Natural rubber)

Preparation of natural rubber

- Natural rubber is made up of a solid particles suspended in a milky white liquid called latex obtained from the cuts of the bark of a rubber tree.
- Latex is diluted and filtered to eliminate any dirt present in it.
- Acetic acid or formic acid is added to coagulate rubber into a white mass
- The coagulated white mass is washed
- It is allowed to pass through rollers to make it soft and flexible

Properties of natural rubber:

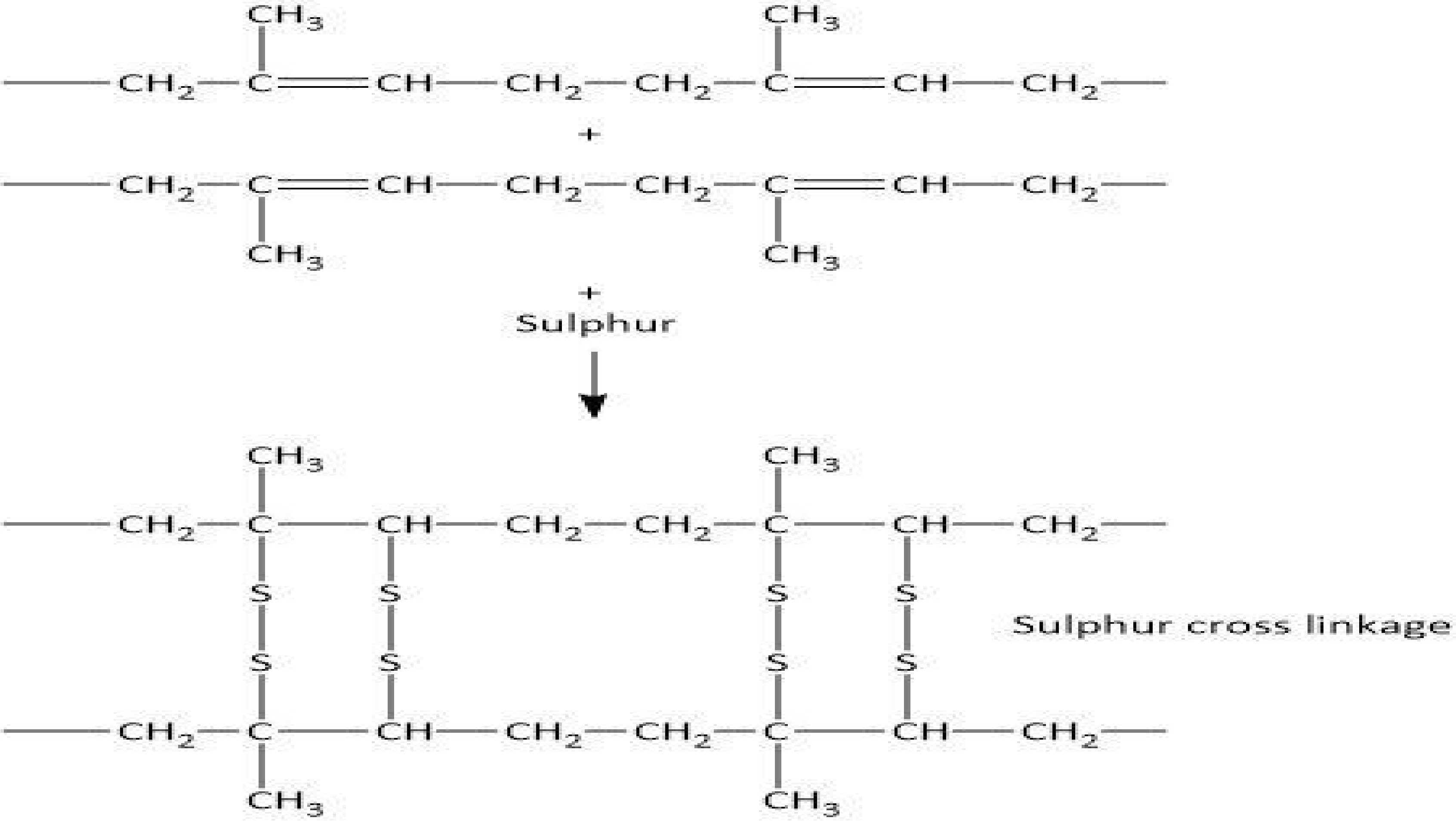
- Soft & sticky
- Flexible
- Low tensile strength
- Plastic in nature
- Sensitive to heat, light
- Low water absorption capacity
- Chemical resistant
- Less resistance to oil, non polar solvents, fats, greases

Vulcanisation of Natural rubber

- Natural rubber is too soft and cannot be used in most of the applications.

  To improve the properties of rubber :

- Natural rubber is heated with sulphur to 140 C
- Sulphur atoms react with the double bonds in the rubber molecule chain to form C-S-S-C cross link between rubber molecules



+
+
Sulphur
Sulphur cross linkage

Advantages of Vulcanised rubber

- High tensile strength
- Excellent resilience
- Low water absorption
- High resistance to oxidation
- High resistance to abrasion
- High resistance to wear and tear
- Better electrical insulator
- Resistant to organic solvents
- Low elasticity

Applications of vulcanised rubber

- Rubber hoses
- Shoe soles
- Toys
- Erasers
- Tires
- Insulating materials
- Rubber lined tanks
- Conveyor belts
- Suction cups
- Rubber seals
- Hockey pucks

Elastomers

Elastomer is a rubbery material composed of long chain molecules that possess the ability to return to its original shape after being stretched.

The molecules of elastomers held together by weak intermolecular forces.

Elastomers have viscosity as well as elasticity therefore they are known as viscoelasticity.

Following are the examples of the elastomers

- Natural rubber: They are used in automotive industry and in the manufacture of medical tubes, balloons, adhesives etc
- Polyurethanes: They are used in the textile industry for manufacturing elastic clothing like lycra.
- Styrene-butadiene rubber(Buna-S): Used as an adhesive, in footwear industry, in electrical insulation.
- Neoprene: These are used in manufacture of wet suits and in industrial belts.
- Silicone rubber: They are used in automotive, electrical, medical, cookware etc

Applications of elastomers

- **Motor vehicles**: Elastomers doesn't melt easily and offers excellent wear resistance making it efficient in building seals, tyres, interior & exterior parts, engine components.
- **Consumer products**: Elastomers has widest range of products starting from shoe soles to baby pacifiers and many more.
- **Construction**: They are used as adhesives and sealants especially for filling the gaps
- **Industrial products**: Elastomers are hugely used in making industrial tools, appliances, belts, molds, lubricants, etc.
- **Wire & cables**: Elastomers provide good insulation, high resistance to heat & easily reshaped therefore they are used to build wires, telecommunication cables.

Conducting polymers

Polymers which conduct electricity are called conducting polymers.

Reason of conduction in the polymer:

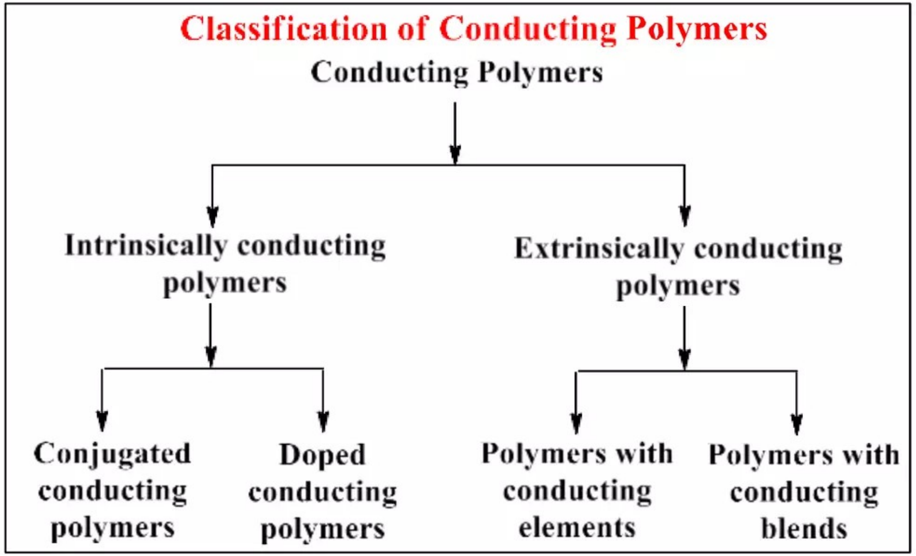
- Presence of unsaturated conjugated double bonds in the polymer
- Addition or removal of electrons (doping) into the polymer

Characteristics:

- Good electrical conductivity
- Easy of preparation
- Light in weight
- Easy to process

Types of Conducting Polymers

- Linear-backbone polymers (polyacetylene, polypyrrole, polyaniline, etc.) **and their copolymers are the main class of conductive polymers.** The different conducting polymers are classified according to their composition. **Table 1** presents some organic conductive polymers according to their composition.



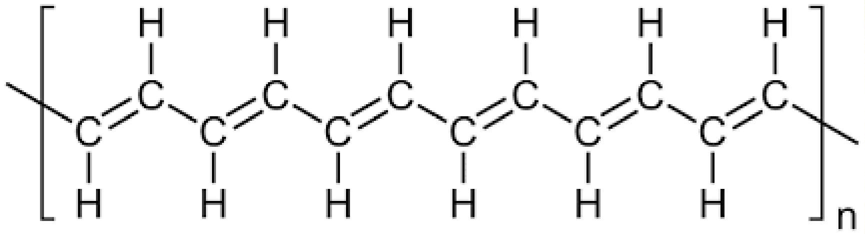
Classification of Conducting Polymers

- Conducting Polymers
  - Intrinsically conducting polymers
    - Conjugated conducting polymers
    - Doped conducting polymers
  - Extrinsically conducting polymers
    - Polymers with conducting elements
    - Polymers with conducting blends

How can a polymer become conducting?

For a polymer to become electrically conductive, it has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms.

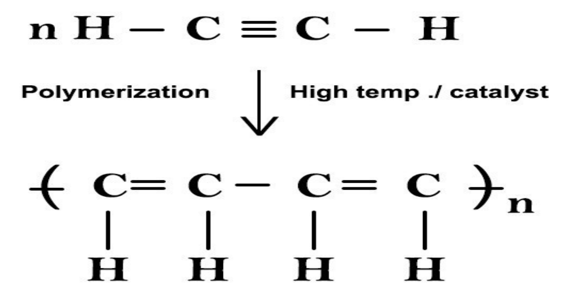
Polyacetylene is the simplest possible conjugated polymer. It is obtained by polymerisation of acetylene. The polymer consists of alternating single and double bonds, called conjugated double bonds.



(In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised “pi” (π) bond which is weaker)

Mechanism of conduction in polyacetylene

Preparation of polyacetylene: Polyacetylene is prepared by passing acetylene gas over Ziegler-Natta catalyst to get polyacetylene.



$$n\,H-C\equiv C-H \xrightarrow[\text{High temp ./ catalyst}]{\text{Polymerization}} \left(\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}} \right)_n$$

The conductance can be improved by either p-doping or n-doping

Types of doping

p- doping:

- Lewis acids or halogens are added to the polymers having conjugated double bonds
- Oxidation takes place
- Creates positively charged sites on polymer backbone, which are current carriers for conduction.
- Examples for p-dopants:

I_2, Br_2, $AlCl_3$, AsF_5, etc.

n-doping :

- Lewis bases or alkali metals are added to the polymers having conjugated double bonds
- Reduction takes place
- Creates negative charged sites on polymer backbone, which are responsible for the conduction
- Examples for n-dopants:

Li, Na, K, tetrabutyl ammonium, etc.

p-doping

It involves two steps

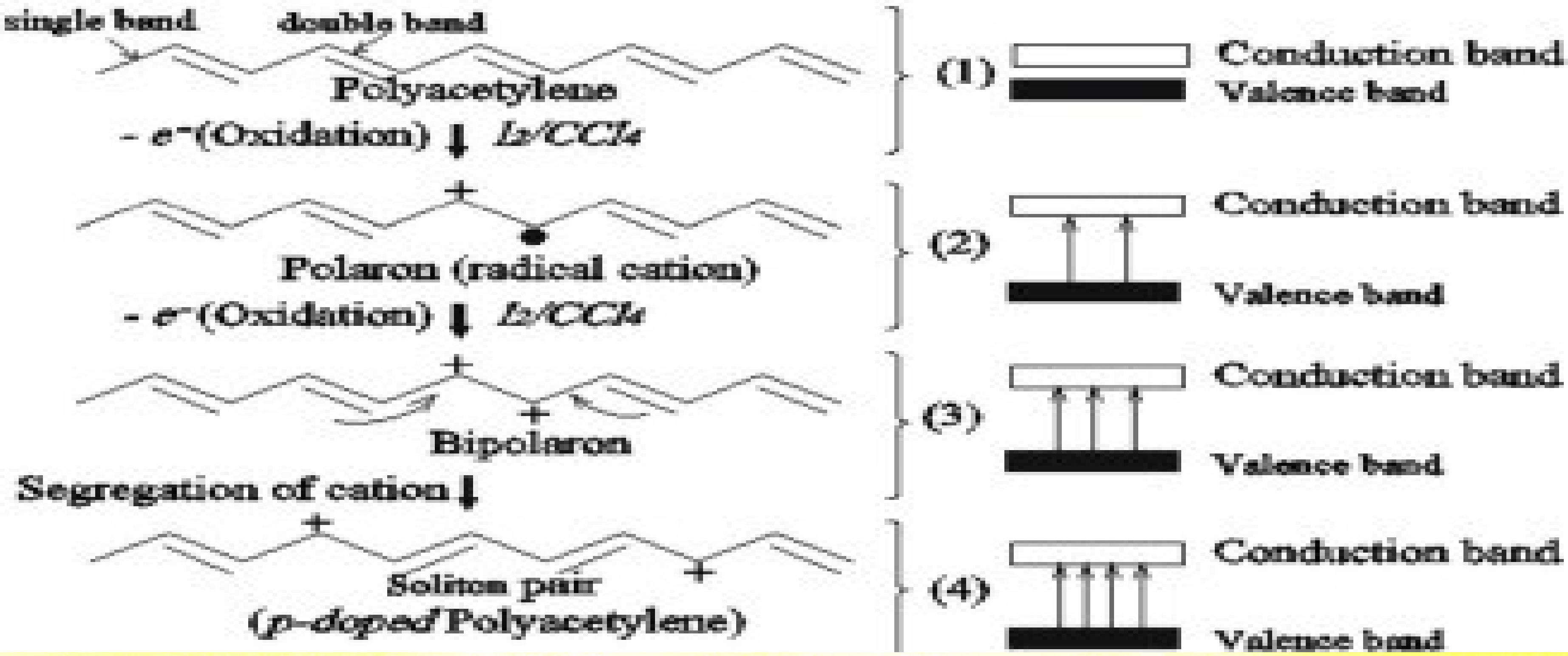
Step I: It involves the oxidation of a polyacetylene with iodine vapour(Lewis acid)

During oxidation the iodine molecule remove an electron from polyacetylene chain creates positive charge called polaron.

Step II: The second oxidation of polaron produces two positive charges on the chain called bipolaron.

This positive charges are mobile due to delocalisation and responsible for conduction.

$$\underbrace{\underbrace{(CH)_x}_{\text{Polyacetylene}} + \underbrace{A}_{\text{Lewis acid}} \rightleftharpoons \underbrace{(CH)_x^{+}\ A^{-}}_{\textit{p-doped}\text{ polyacetylene}}}_{\text{Oxidation process}}$$



n-doping

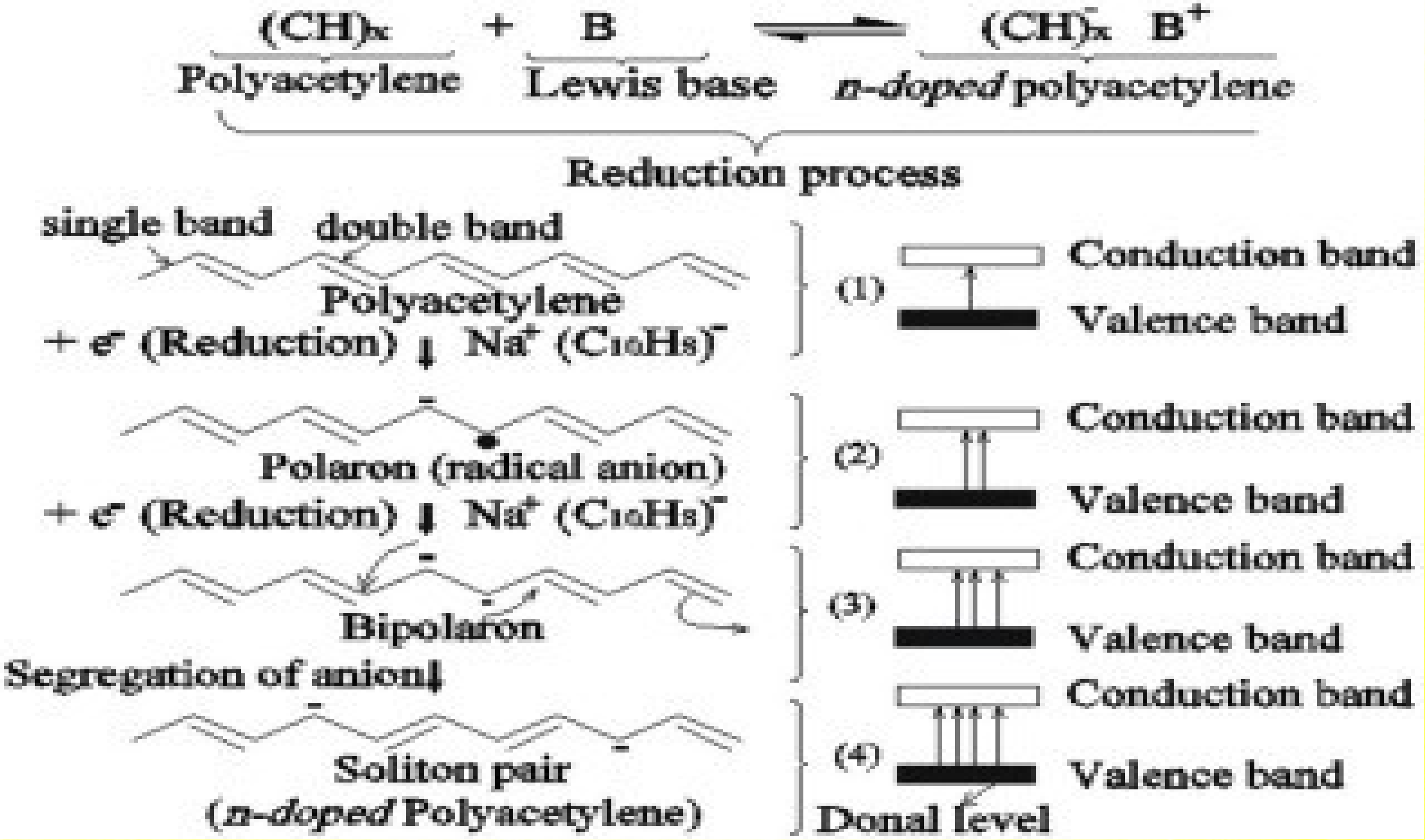
It involves two steps

Step I: It involves the reduction of polyacetylene of with sodium naphthalide

During reduction sodium naphthalide donates an electron to polyacetylene chain creates negative charge on the chain called polaron.

Step II: The second reduction of polaron two produce two negative charges on the chain called bipolaron.

This negative charges are mobile due to delocalisation and responsible for conductance.


(CH)x + B ⇌ (CH)x⁻ B⁺
Polyacetylene
Lewis base
n-doped polyacetylene
Reduction process
single band
double band
Polyacetylene
+ e⁻ (Reduction) ↓ Na⁺ (C10H8)⁻
Polaron (radical anion)
+ e⁻ (Reduction) ↓ Na⁺ (C10H8)⁻
Bipolaron
Segregation of anion ↓
Soliton pair
(n-doped Polyacetylene)
(1)
(2)
(3)
(4)
Conduction band
Valence band
Conduction band
Valence band
Conduction band
Valence band
Conduction band
Valence band
Donal level

Applications of conducting polymers

- Incorporated into commercial displays and batteries
- Printed electronic circuits
- Organic light emitting diodes
- Supercapacitors
- Chemical sensors
- Used in solar cells
- Electromagnetic shielding
- Flexible transparent displays
- Microwave absorbing coating
- Radar-absorptive coating on stealth aircraft

Biodegradable polymers

Polymer that can be decomposed by the action of microorganisms are called biodegradable polymers

These polymers broken into small segments by enzyme catalysed reactions, and microorganisms produce this enzymes.

Examples of biodegradable polymers are polylactic acid, polyvinyl alcohol

Poly lactic acid

Advantages:

- Easy to process
- Bio compatible
- Biodegradable plastic
- Good plasticity
- Low cost
- Rigidity

Applications:

- Medical implants like stents
- Implantable drug dispenser
- Food packaging
- Disposable tableware
- Compost bags

Poly vinyl alcohol

Advantages:

- High chemical stability
- High thermal stability
- Low manufacturing cost
- Excellent water resistant
- High strength

Applications:

- Paper making
- Contact lenses
- Absorbable sutures
- Drug delivery systems
- Artificial heart surgery
- Cartilage replacements

Properties biodegradable polymers

- Biodegradable polymers can retain good mechanical integrity until degraded.
- Since biodegradable polymers have extremely strong carbon backbones that are difficult to crack, degradation begins at the end-groups.
- Biodegradable polymers are non toxic
- Degradation rates can be regulated
- Biodegradable polymers are hydrophilic

Uses of biodegradable polymers

Used in

- Controlled drug release systems
- Plasma replacements
- Agricultural materials such as films & seed coatings
- Fast food wrappers & personal hygiene products
- Drug delivery
- Post operative stitches

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UNIT IV
ENERGY RESOURCES

Fuel:

Any material that can be burned to release thermal energy. Most familiar fuels consist primarily of hydrogen and carbon. They are called hydrocarbon fuels and are denoted by the general formula $CnHm$. Hydrocarbon fuels exist in all phases, some examples being coal, gasoline (usually treated as octane $C8H18$), and natural gas.

Classification of chemical fuels;-

These are two types, Primary fuels – found in the nature .Secondary fuels—which are obtained from primary fuel.

Fuel physical state	Primary (or)natural fuels	Secondary (or) synthetic fuels.
• solid	Wood ,peat ,lignite, coal	Coke, semi coke, char coal
• liquid	Petroleum(crude oil)	Coal tar, petrol, deasil.
• gas	Natural gas	Coal gas, water gas, producer gas

UNIT IV
ENERGY RESOURCES

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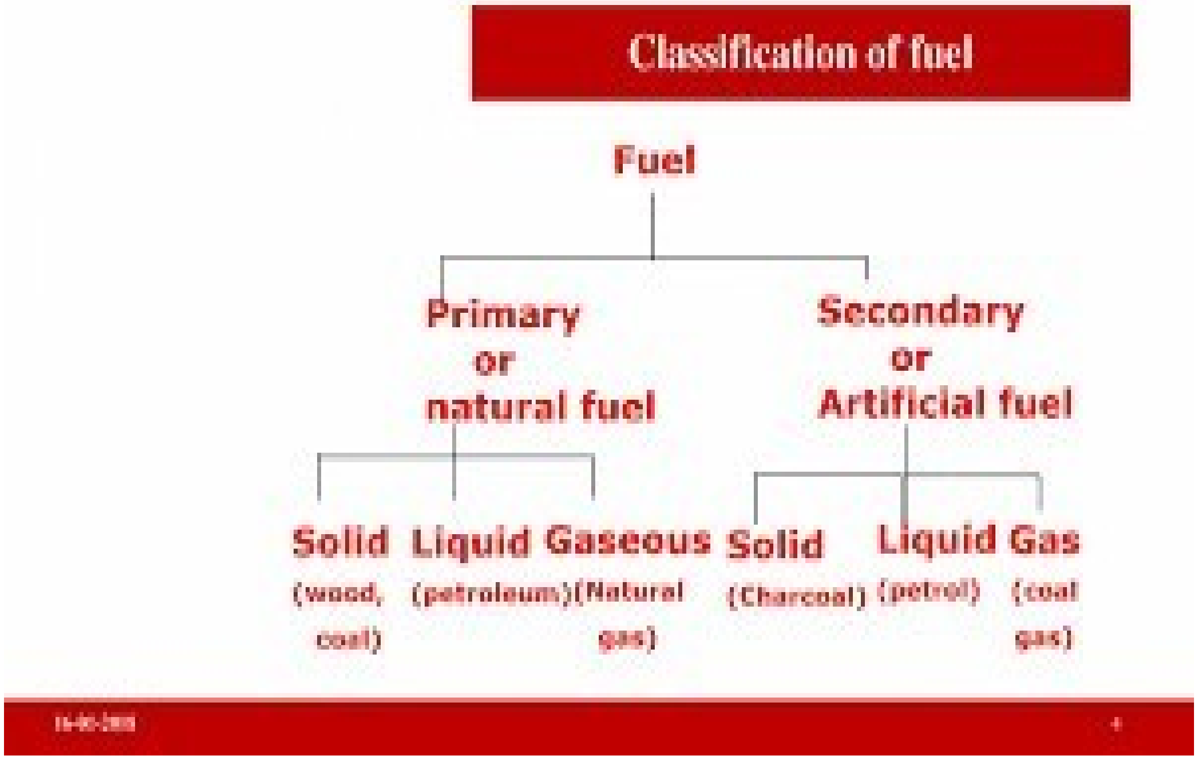


Classification of fuel

Fuel

Primary or natural fuel

Solid (wood, coal)

Liquid (petroleum)

Gaseous (Natural gas)

Secondary or Artificial fuel

Solid (Charcoal)

Liquid (petrol)

Gas (coal gas)

Calorific value: - The amount of heat obtained by a complete combustion of a unit mass of a fuel. Fuel calorific value is two types:-

- Gross calorific (or) higher calorific value (H.C.V)
- Net calorific value (or) lower calorific value (N.C.V)

Gross Calorific Value – (G.C.V) :-

- It is the total amount of heat produced when Unit mass of fuel is completely burned without elimination of latent heat of water vapour.

Net Calorific Value – (G.C.V) :-

N.C.V = gross calorific value – latent heat of vaporization.[Mass of hydrogen per unit weight of fuel burnt ×9× latent heat of vaporization of water]

one part of H gives 9 parts of H_2O and latent heat of stream for water is 58 7 cal/g.

N.C.V = G.C.V- 9×(H/100)×587 (Or)

Where H= % of Hydrogen in the fuel)

N.C.V = G.C.V – 0.09×H×587

Solid fuels.

Analysis of Coal: - To assessment the quality of coal is proved by the following to analysis.

1. **Proximate analysis** 2. **Ultimate analysis**

Proximate Analysis of Coal : - Based on the determination **of % of moisture, volatile matter, ash and fixed carbon** in a given whole sample. This information gives to estimate the quality of coal.

Moisture :-Step-1 1 gm of air dried coal powder taken into crucible which is heated on electrical oven at 105 °C for 1 hour after cool in desiccators cool and weight out the weight loss represented as %moisture

%moisture =loss in weight of coal/weight of coal taken×100

Volatile matter:

Step-2: dried coal left in crucible from step1 covered with lid which is heated on muffle furnace at 950c for 7 minutes and cool in desiccators and weighted out and the weight loss represented as % volatile moisture.

% volatile matter = loss in weight due to removal of volatile matter/weight of coal taken ×100

Ash: Step-3 the residual sample in crucible from step 2 which is heated again muffle furnace at 700 to 750 Oc The weight loss is represented as

%ash=weight of residual/weight of coal taken×100

FIXED CARBON – Fixed carbon is determined by the following equation

% of fixed carbon = 100 - (% of the moisture + volatile matter + ash)

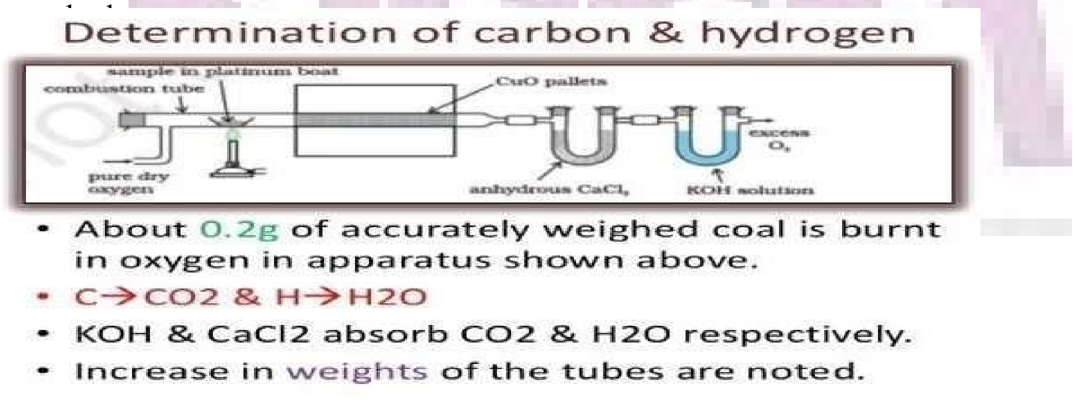
Good quality of coal has more fixed carbon

Ultimate analysis of coal

Ultimate analysis of coal is determined by % of compositions of the elements or constituted of elements of carbon, hydrogen, nitrogen, sulphur, oxygen and ash content

Carbon and hydrogen % determination

- 1 -2 gm of coal sample is burnt in oxygen the coal sample containing carbon to give CO2 and hydrogen to give water by the combustion.
- CO_2 passed through the KOH capillary Bulbs there by increased weight of that bulb corresponding to % of carbon
- H_2O is passed through $Cacl_2$ bulb there by increased weight of that bulb corresponding to % of


Determination of carbon & hydrogen

- About 0.2g of accurately weighed coal is burnt in oxygen in apparatus shown above.
- C→CO2 & H→H2O
- KOH & CaCl2 absorb CO2 & H2O respectively.
- Increase in weights of the tubes are noted.

$$2KOH+CO_2 \rightarrow K_2CO_3+H_2O$$

$$CaCl_2+7H_2O \rightarrow CaCl_2.7H_2O$$

%carbon = increased in weight of KOH tube/weight of coal taken× □□/□□

%hydrogen = increased weight of $CaCl_2$ bulb/weight of coal taken× □/□□

Nitrogen: % of nitrogen in coal determined by kjeldahl method

- A known weight of 1gm of coal powder is taken in kjeldah flask which is oxidation by heating **with H_2SO_4+K_2SO_4 and $HgSO_4$** to get clear solution of ammonium sulphate
- ($(NH_4)_2SO_4$ which is followed the heating with KOH to liberate the ammonia (NH_3) and added a known volume of Hcl
- Which is titrated against with NaoH the amount of acid neutralised by liberated ammonia to determine the nitrogen

% of nitrogen =volume of acid consumed ×normality of acid× □□ × □□□ / weight of coal taken × □□□□

Sulphur: sulphur is present on coal is estimated by gravimetrically

A known coal sample burnt in bomb calorimeter, if sulphur is present to give sulphates, sulphides

etc, which are followed the treatment with $Bacl_2$ to give the barium sulphate precipitation, and it is dried out and weighed out

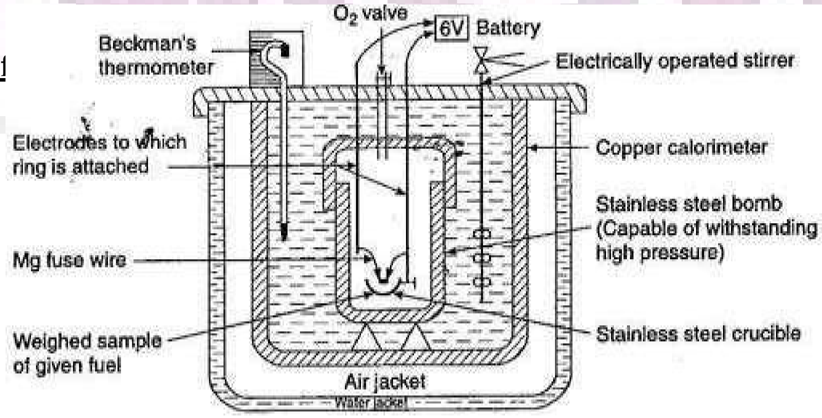
% of the sulphur=weight of $Baso_4$× □□ × □□□/weight of coal taken × □□□

Ash:% of ash=weight of ash residue /weight of coal taken× 100

Oxygen: the percentage of oxygen is determined by subtracting sum of the percentage of C,H,S and ash from 100 % O = (100- SUM of % C+H+N+S+ASH)

% oxygen=100 - % of (C+H+N+S+Ash)

Determination of **rimeter**



- it consists of three racks(vassals) 1.steel bomb 2.copper calorimeter 3.Air jacket
- Steel bomb has tight with lid which contain two steel electrodes are connected to battery
- Steel bomb vessel is inserted into the copper calorimeter which contain the water, stirrer and Beckmann thermometer
- Coper calorimeter is also inserted into air jacket its main function to prevent the heat from outside

Procedure:

- Take a known mass (0.5-1gm) of the given fuel into crucible
- mg wire touch with sample passing the current through the electrodes
- Burning of the sample by the presence of o_2 inside the steel bomb by the result of to release the heat
- liberated Heat from fuel is transferred to cu calorimeter there by water is heating slowly, when water temperature will get highest temperature recorded in thermometer which is indicated that fuel grass calorific value

Calculation:

X=mass in gram of fuel taken crucible

W=mass of water in the calorimeter

w=water equivalent of the calorimeter, bomb, thermometer, stirrer

t1=initial temperature of water in calorimeter

t2=final temperature of water in calorimeter (after combustion)

l = higher calorific value(gross calorific value)

heat liberated by burning of fuel=(W+w) (t_2-t_1)

but heat liberated by fuel=heat absorbed by water apparatus

XL= (W+w) (t_2-t_1)

HCV of the fuel of= (W+W)(t2-t1)/X

Hence LCV=(L-0.09×H×587)Cal/gm

LIQUID FUELS

PETROLEUM

- Petroleum (fossil fuel or crude oil): it is the best primary liquid fuel---found in the deep earth crust (Petr a= rock, oleum = oil) -----it is a brown viscous liquid
- it is the mixture of hydro carbons(paraffin ,aromatics ,naphthalene , nitrogen ,sulphur, oxygen

- The composition of crude oil is ->c-80-87%,s-0.1-35%,n-0.4-0.9%,h-11-15%,o-1-0.9%
- Refining of crude oil: Refining of crude oil involves the three steps:

Step-1:

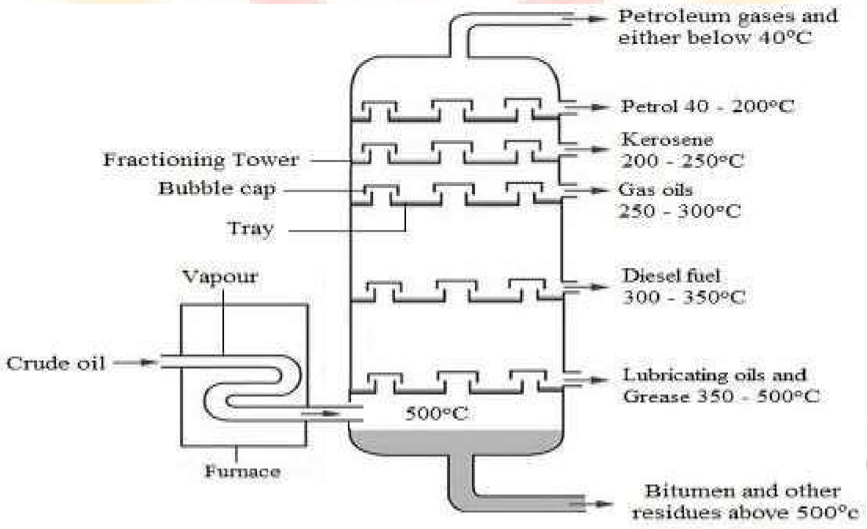
separation of water by coteril's method:

- The crude oil as an emulsion of oil and water .water is separated by using of highly charged electrodes ,the colloidal water is separated from oil in the form of big droplets by high current

Step-2:

- **removal of sulphur compounds:**

Crude oil is treated with copper oxide (cu_2o) which gives black ppt o (cus↓) copper sulphte



Step3: fractional distillation:

- Fractionating column consist of pipe still and bubble tower
- Bubble tower is a tall cylindrical tower containing number of horizontal trays, each tray provided the chimney, and covered with loose cap

- The crude oil is heated to 400℃ in furnace (pipe still), converts into vapour
- The hot vapours are then passed into a fractionating column,
- As the vapours go up , through the chimney they become gradually cooler and fractional

  condensation takes place at different height of column

- Higher boiling point fractions condense first at lower part while lower boiling fractions condense above column. vapours, turn by turn different fractions are separated out at their corresponding boiling points

Rocket fuels:

- Fuels which burn quickly and give a very large volume of gases to propel a rocket are called rocket fuel or propellants
- they are either high oxygen -containing fuels or mixture of fuel
- An oxidant the propellants reacts very quickly producing a very large volume of gases at a temperature of 3000c and a pressure of 300kg/cm
- The gases exit through a small opening call nozzle at supersonic velocity this act of pushing the gas backward produces equal force acting in the opposite direction which move the rocket forward rockets are used for putting space capsule into orbit and hurling explosives

Solid propellants:

- EX: mixture of nitro cellulose and nitro glycerine
- mixture of nitro cellulose and nitro glycerine

Liquid propellants:

- EX: hydrogen peroxide, nitro methane, ethylene oxide, hydrazine, propyinitrite and mixture of methanol and hydrogen peroxide

Cracking:

Cracking is the process of conversion of bigger hydro carbon molecules into smaller hydro carbon of lower molecular weights (Decchene is cracking into pentane and pentene)

Ex: $C_{10}H_{22} \rightarrow C_5H_{12} + C_5H_{10}$

Process of cracking brings about

1. The conversion of high boiling fractions into low boiling fractions into boiling fractions suitable for automobile 2.production of raw material for petrochemical industries

Cracking is mainly divided into two types -1.**Thermal cracking 2.Catalytic cracking**

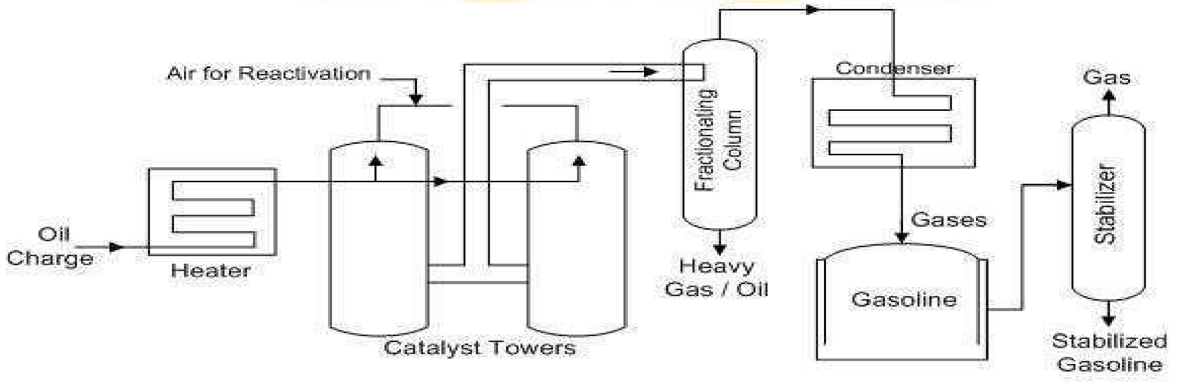
Catalytic cracking: in this type cracking catalysts are used:

- Suitable catalyst likes aluminium silicate, Al_2O_3, etc. by this catalyst cracking quality and yield of **Gasoline (petrol) are produced. By this Cracking process**

There are two types of catalytic cracking

1. **Fixed bed catalytic cracking** 2 . **moving bed catalytic cracking**

1. Fixed bed catalytic cracking:

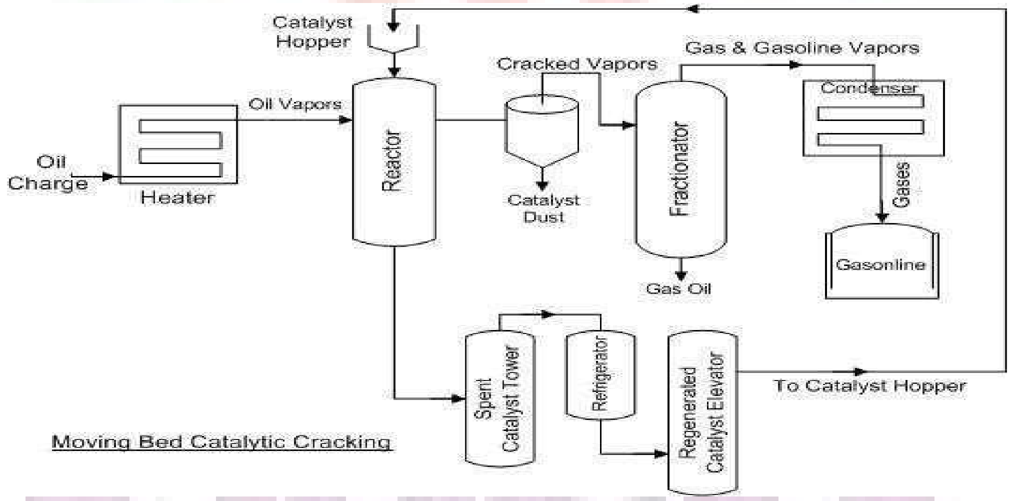


Fixed Bed Catalytic Cracking

- The oil vapour are heated in pre heater about 425-450°
- The hot vapours are forced to catalyst chamber (containing artificial clay+zro_2) maintained at 425-450° and 1.5 kg/wt produced
- Cracking is taken place on catalyst bed 40%carge converted into petrol and along with 2-4% carbon dust produced dust deposit over the catalyst
- Cracked vapours produced are then passed through a fractionating column where heavy oil fractions are condensed
- The vapours are then passed through cooler where some gases are condensed along with gasoline uncondensed gases move on stabilizer where dissolved gases are removed and pure gasoline is obtained
- due to deposit of carbon dust over the catalyst bed otter 8-l0hour stops functioning bed is re activated by burning of carbon dust

2. Moving bed catalyst process (fluid-bed cracking)

- In this process the solid catalyst is finely powered which act as a liquid and is circulated in gas stream
- Heavy oil vapours and catalyst fluid are allowed into reactor 500℃ cracking is the takes place , near top of the reactor there is centrifugal separator,which can allow only cracked vapours but not catalyst powder and carbon dust
- Cracked vapours passed through fractionating column and heavy oil separated , formed vapours are sent to cooler gasoline is separate out along with uncondensed gases move on stabilizer
- Carbon coated catalyst reached at bottom of reactor and sent into regenerator and burnt at 600℃ carbon dust elevated as co_2 and to produce freshly regenerated catalyst is reused



Moving Bed Catalytic Cracking

Synthetic petrol or gasoline prepared by to process:

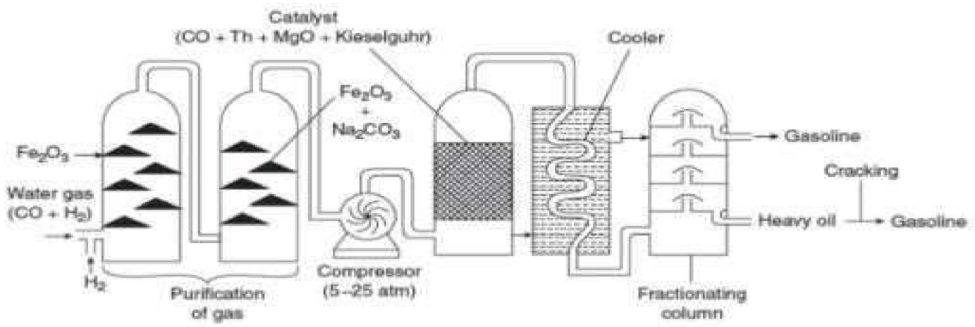
1. Fisher tropsch method 2. **Bergius process**

1. Fisher tropsch method for synthetic gasoline (petrol)

- water gas is mixed with H_2 gas, passed into purification towers to remove the H_2s and organic sulphur

- Purified gas is compressed at 5 to 25 atm are passed into converter containing catalyst mixture(a mixture 100 parts Co+5part thoria+8parts magnesia +200 parts kcisal gargh parts solution of earth) maintains at 200-300℃
- A mixture of saturated and unsaturated hydro carbons formed in the convertor
- $nCo+2n\ H_2\rightarrow c_nH_{2n}+n\ H_2O$--------- olefins
- $c_nH_{2n}+H_2\rightarrow c_nH_{2n}+2$---------- paraffin
- Hot gas mixture passed into passed into a cooler where liquid resemble crude oil is obtained
- Crude oil sent into fractionating column to get gasoline and heavy oil, the heavy oil reused for cracking to get more gasoline

Fischer–Tropsch Process



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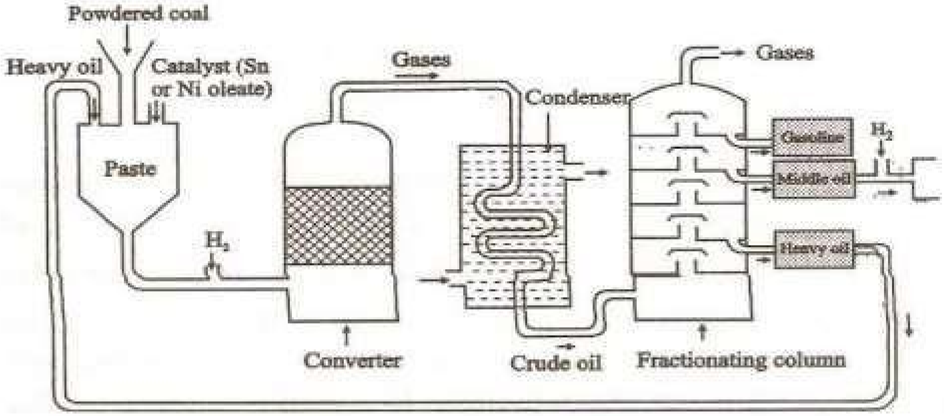
Engineering Chemistry (revised edition)
ISBN: 978-81-265-4475-2

2. Bergius process for Synthetic Petrol



- It is done by hydrogenation of coal
- low ash coal is powdered and mixed with catalyst (Ni) and made past by mixing with heavy oil
- The paste mixed with H_2 gas and then sent through the converter which is maintained at 350-500° and 200-250°
- The combustion of H_2 with carbon coal to give hydrocarbon gases where liquid resembling the crude oil
- The gases coming out the convertor to pass the fractionating column where gasoline is obtained along with middle oil and heavy oil obtained.
- Middle oil and heavy oil are undergone by hydrogenation to give gasoline and heavy oil fraction as recycled to make as paste with coal powder

Internal combustion Engine properties:

1. Knocking
2.antiknocking
3.octane number
4.cetane number

Knocking:

- Knocking is un desirable properties of internal combustion engine
- When compression ratio is exceed then the normal way (to increase the rate of oxidation)
- By the result of to raise the temperature that causes for combustion of fuel before touch the spark ignition
- So that flame (combustion) leads to irregularly. randomly or,un uniformly thereby there is rattle sound generated the inside cylinder which is called knocking.
- Due to this property to reduce the piston life and damage the cylinder ,more consumption of fuel,
- This is mainly cause, to use the straight chain hydro carbon in petrol (chemical structure of hydro carbons)

Preventing the knock:

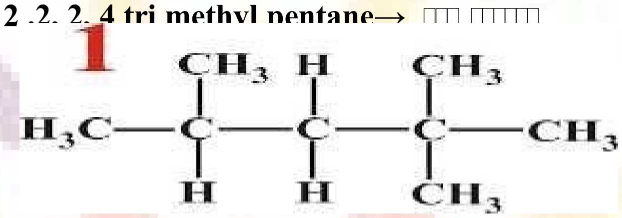
1. Good quality of fuel with higher octane number 2.by adding anti knocking reagents

3. by the retarding sparkplug ignition

Octane number:

- It is to be decided the quality of petrol it is introduced by edger he has to prove taken two components in gasoline
- n heptane → **CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3** (**It shows 100% knocking (octane number=0**)

1. 2 ,2, 2, 4 tri methyl pentane→ □□ □□□□□



(It shows 0% knocking (octane number=100)

Octane number: Percentage of iso octane in mixture of isooctane+ heptanes

Octane Number = 80 means 80% iso Octane and 20% n heptane

The given fuel % n heptane - shows knocking

% iso

octane- shows

octane number

Anti knocking reagents:

- Anti knocking reagents are added to straight chain hydro carbon petrol, which converts into branched chain hydro carbons there by knocking is reduced
- Petro anti knocking reagents are anti knocking reagents are – $(C_2H_5)_4Pb$ tetra ethyl lead
- $(C_2H_5)_4Pb$ dissociate to give $C_2H_5^-$ and $Pb^{+\ 2}$radicals
- C_2H_5 able to attack the straight chain hydro carbon to converts into branched chain carbon
- During this process pb^{+2} is left over, which is poisoned and can be eliminated it by adding of C_2H_5Br
- C_2H_5Br is dissociated to give C_2H_5 +Br^- of the Br^- reacts with pb to give $pbBr_2$ volatile

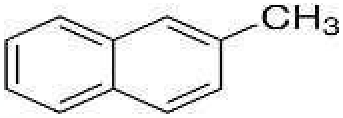
Cetane number:

It is to be decided that the quality of diesel when diesel oil contain the branched chain hydro carbon shows knocking

Disel Knocking:

If branched or cyclic hydro carbon chain present in diesel (**2 methyl naphthalene)** it gives bad knocking but it contain straight chain hydrocarbon (**CH_2-(CH_2)$_{14}$-CH_2**) does not exhibit the knock.
It is explained by use of the following compounds

Cetane – **CH_2-(CH_2)$_{14}$-CH_2 Hexadecchane**



2 methyl naphthalene

Cetane number= % **of cetane in mixture of cetane+2 methyl naphthalene**

Ex: cetane number 60 means - 60% cetane 40 % 2methyl naphalene

It gives 40% knocking

Anti knocking reagents for diesel:

Anti knocking reagents like CH_3-CO-CH_3, C_2H_5 No_2 are added to diesel which contain cyclic structure are opened ring by ant knocking reagents to converts into straight chain hydrocarbon to reduce the knocking

Natural gas:

Natural gas primarily methane gas It is fossil fuel. it is two type:

1. Dry or lean gas: the natural gas contain CH_4 lower hydrogen carbons like C_2H_6, C_3H_8etc--- CH_4
2. Wet or reign gas: natural gas contain higher hydro carbons present

Natural gas composition:

It consists of 70 to 90%- CH_4, 5-10% ethane, 3-1 % H_2 and react of Co and Co_2 its calorific value 12000-14000 kcal/m

Uses:

1. Used as a domestic fuel, raw material in carbon block manufacture
2.It is used for manufacturing different synthetic chemicals
3. It is used in preparation of compressed natural gas
4. Due to less in preparation it is good substitute for petrol and diesel

L.P.G : (LIQUID FIELD PETROLEUM GAS)

1. The main components of l PG gas are n butane ,isobutene ,butylenes, and propane

2.The gas can be compressed under pressure in container and sold trade flames like Indian, hp, bharat gas etc---

3.The gas is obtained from natural gas or as a by product in refineries during cracking of heavy petroleum product

4.its calorific value -27000 kcal/m^3

Advantages of LPG

5. LPG is used as domestic fuel and as fuel for internal combustion engine

6.it is used in hydrolysis process

7.LPG is used in industries as welding annealing ,cutting cl$^-$

C.N.G (compressed natural gas):

8. When natural gas (CH_4) is compressed at high pressure (1000 atm) or cooled to -160°□ it is converted in CNG

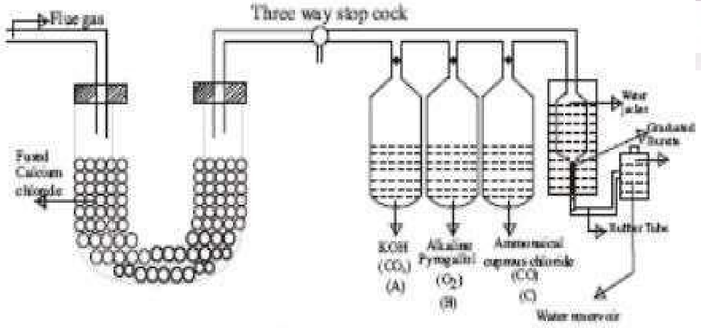
9.it is stored in cylinder made of steel

10.it is now replacing gasoline (petrol) as it releases less pollutants during combustion c.n.g vehicles are used to reduce the pollution

Advantages:

1. Due to high of ignition CNG is better than petrol and diesel
2. It releases least pollutants like Co and un burnt hydro carbons
3. Operating cost of CNG is less, and easily stored
4. It undergo regular combustion

ANLYSIS OF FLUE GASES BY ORSAT'S APPARATUS:



Flue gas analysis

- Flue gases is mixture of **CO_2 CO, O_2** exhausted from combustion chamber
- Analysis of flue gases the idea about complete or incomplete combustion process
- After combustion gases coming out **CO_2 CO O_2** these are called flue gases

- in the case of **complete combustion** to evolve the Co2 gas, If **incomplete combustion** to evolve the Co will be more due to insufficient o^2 , Excess oxygen supply to evolve the xygen , it means more oxygen is supplied for combustion

- Orsat's apparatus is used for the flue gas analysis

- the apparatus has measuring with water jacket there are 3 absorption bulbs fitted with stop clocks and connections to measuring burette

- the bulbs are connected to **u tube** glass wool and fused $cacl_2$ which is to avoid incoming smoke particles to come in water jacket maintenance constant temperature in burette out of three
- bulbs

first Bulb has koH solution which is absorbed the Co_2 in flue gases,

- The second bulb has alkaline pyrogallic acid which absorbs**O_2** and also absorb(CO_2 if present)

- Third bulb has amonical $Cucl_2$ acid it can absorb **CO** and -(O_2,Co_2 if present)
- . After each absorption in three bulbs the gas is sent from burette and the volume of gas is measured at room temperature the decrease in volume after each absorption corresponds to the volume **CO_2 CO, O_2** in three bulbs the quantitative analysis of flue gas observed is made gas chromatography
- 12. The gas remaining in tube burette after absorption **Co_2 Co , O_2** is taken as N2, knocking the volume of gases observed and the volume of original gases ,There % can be calculated.

% of the gas in the bulb => g= a / mv ×100.

a. Where a=amount of the gas in the bulb. m=mass of the gas in the
b. bulb. V=total volume of the gas in the bulb.

Power alcohol;-

- Power alcohol fuel is i=used in powered car was made in china .in 1935
- ethyl alcohol is used in internal combustion engine as fuel it is called power alcohol
- Generally power alcohol 5-25% alcohol is mixed with petrol, and along with small percent of benzene
- Power alcohol has good anti knocking property with octane number =90 while petrol octane number =65

Advantages:

- Increases the octane number of petrol
- Alcohol has a property of absorbing of water if present in pentane
- Power alcohol is cheaper than petrol

Disadvantages:

- While power alcohol is used up to 35% power output is used
- Oxidation of ethyl alcohol produced acetic acid which causes corrosion to engine parts
- When power petrol is used to cause the starting troubles of making due to higher surface tension

Bio-diesel:

- Bio diesel is chemically very similar to diesel and is produced by **transesterification of vegetable oil**
- Biodiesel molecules are long chain carbon atoms containing an ester group at one end. But diesel molecules does not have ester group
- Diesel engines can burn biodiesel fuel with no modification
- Vagatable oil molecules is three types larger than normal diesel molecules
- The large size of veg oil causes gels in cold weather this gel formation is prevented by biodiesel process. During this process elimination of H_2O molecules otherwise to form soaps

UNIT V

CEMENT

Concrete is widely used as a non-metallic material in construction of buildings, dams, bridges, high ways etc.

In concrete, cement is a building material that possesses cohesive and adhesive properties and capable of bonding with stones, bricks, building blocks etc.

Portland cement: The name Portland cement is used because this powder on mixing with water gives a hard, stone like mass which resembles Portland rock (Leeds city UK).
It is widely used as a non-metallic material in construction.
It is a composition of calcium silicates, calcium aluminates and small amount of gypsum.

Composition of Portland cement:- A sample of Portland cement contain following composition:

i) Calcium Oxide or lime (CaO) : 60-70%
ii) Silica (SiO_2) : 20-24%
iii) Alumina (Al_2O_3) : 5-7.5%
iv) Magnesia (MgO) : 2-3%
v) Ferric Oxide (Fe_2O_3) : 1-2.5%
vi) Sulphur trioxide (SO_3) : 1-1.5%
vii) Sulphur Oxide (Na_2O) : 1%
viii) Potassium Oxide (K_2O) : 1%

Setting and Hardening

When water mixed with Cement, form a plastic paste.
The past is subjected to hydration and gel and finally crystalline products are formed.

$3CaO.Al_2O_3 + 6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O$ + Heat

$2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.6H_2O + Ca(OH)_2$ + Heat

$4CaO.Al_2O_3.Fe_2O_3+7H_2O \rightarrow Ca_3Al_2O_6.6H_2O + CaO.Fe_2O_3.H_2O$ + Heat

Tobermonite gel, calcium hydroxide crystallization and hydrated tricalcium aluminate are responsible for final setting and hardening of cement.

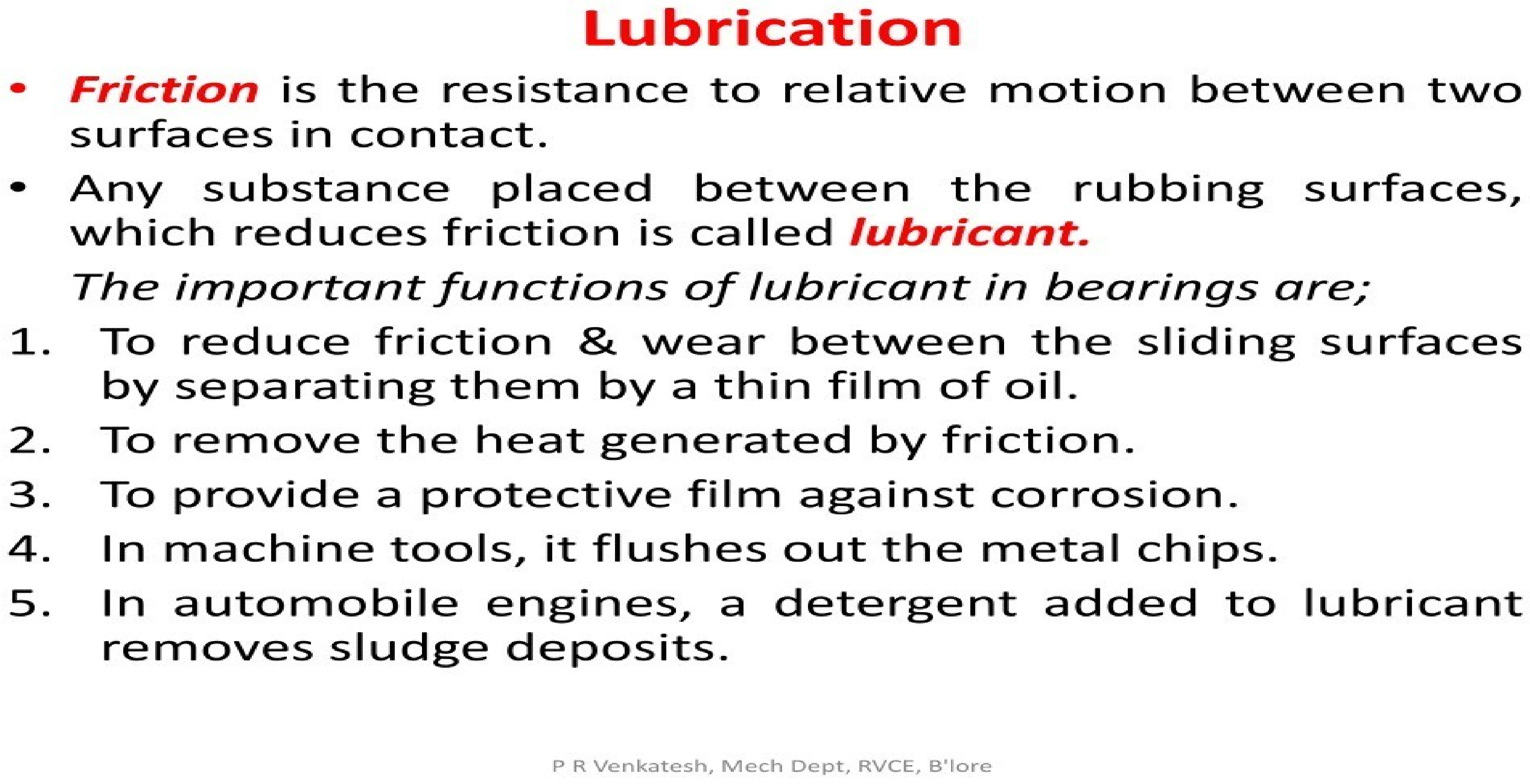
$2(2\ CaO.SiO_2) + 6H_2O\ 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$ + Heat

$3CaO.Al_2O_3 + 6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O$ + Heat

Role of gypsum: 2-3% of gypsum is added to prevent the early setting of cement.

$3CaO.Al_2O_3 + xCaSO_4.2H_2O\ 3CaO.Al_2O_3.\ xCaSO_4.2H_2O$

UNIT V
ENGINEERING MATERIALS



Lubrication

- ***Friction*** is the resistance to relative motion between two surfaces in contact.
- Any substance placed between the rubbing surfaces, which reduces friction is called ***lubricant.***

The important functions of lubricant in bearings are;

1. To reduce friction & wear between the sliding surfaces by separating them by a thin film of oil.
2. To remove the heat generated by friction.
3. To provide a protective film against corrosion.
4. In machine tools, it flushes out the metal chips.
5. In automobile engines, a detergent added to lubricant removes sludge deposits.

P R Venkatesh, Mech Dept, RVCE, B'lore

Types of Lubricants

Lubricants are classified as;

(i) Liquid lubricants

(ii) Semi-liquid lubricants

(iii) Solid lubricants.

Liquid lubricants may be

mineral oils (produced from refining of petroleum products)

synthetic oils (produced from sand, coal, etc.)

Animal & vegetable oils (fish oils, lard oil, Castor oil, cotton seed oil, Olive oil, etc.)

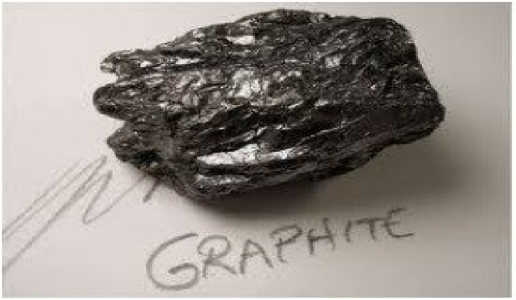
Liquid Lubricants

Semi Liquid Lubricants

- ***Semi liquid lubricant or Grease*** is obtained by compounding the petroleum products with soap mixtures.
- They are highly viscous. They can withstand high pressure, temperature and also they resist corrosion.
- They are used in gear drives, chain drives, flexible cables, etc.
- They may be of Aluminium base, Calcium base, sodium base or mixed base types.

Greases

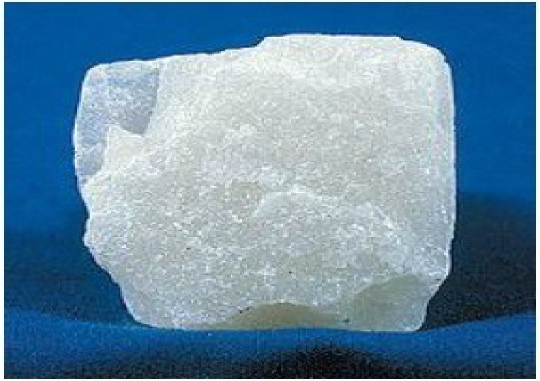
Solid Lubricants



Graphite

Soap Stone

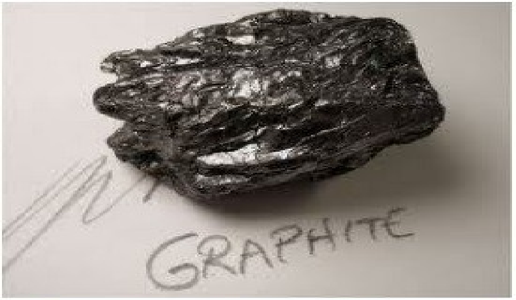
Mica



Talc

French Chalk

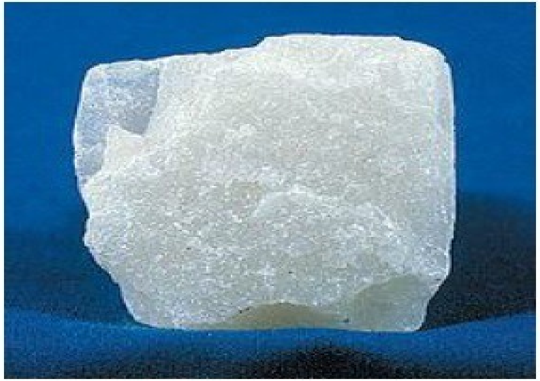
Solid Lubricants



Graphite

Soap Stone

Mica



Talc

French Chalk

Properties of Lubricants

The following are the important properties of a lubricant.

Viscosity:

- It is the property of a fluid by virtue of which it offers resistance to shear (flow).
- If the viscosity is too low, a liquid film can not be maintained between the moving surfaces.
- On the other hand, a high viscosity oil will offer greater resistance to moving parts.
- The viscosity decreases with increase in operating temperature.
- ***A good lubricant, the change of viscosity with temperature must be a minimum.***

Types of viscosity

Viscosity of a lubricant may be defined by

(i) Absolute (or Dynamic) Viscosity (m)

- It is the force required to move a surface of unit area at unit velocity when separated by an oil film of unit thickness.
- In SI system, unit of absolute viscosity is N-sec/m^2 (Pascal-sec)

(ii) Kinematic Viscosity (n)

- It is the ratio of absolute viscosity to mass density of the fluid. Its SI unit is m^2/sec.

i.e

Flash Point:

- Flash point is the minimum temperature at which an oil gives off sufficient vapour to ignite momentarily on introduction of flame.
- A good lubricant must have its flash point ***above the operating temperature.***

Fire Point:

- Fire point is the lowest temperature at which an oil gives off sufficient vapour to burn continuously when bought in contact with a flame.
- A good lubricant must have ***a high fire point.***

Pour Point & Cloud Point:

- Pour point is the lowest temperature at which an oil ceases to flow when cooled.
- Cloud point is the lowest temperature at which wax and other substances crystallize and separate out when cooled.
- A good lubricant must have ***a low pour & cloud points.***

Carbon residue:

- Lubricating oils contain higher percentage of carbon in the combined form. At high temperatures, they decompose resulting in carbon deposits on bearing surfaces which is undesirable.
- ***A good lubricant should not decompose even at high temperatures.***

Mechanisms of Lubrication

1. Fluid-film (or) Thick-film (or) Hydrodynamic lubrication
2. Boundary lubrication (or) Thin-film lubrication
3. Extreme pressure lubrication

1. Fluid Film/Thick-Film/Hydrodynamic Lubrication (~ 1000 Å)

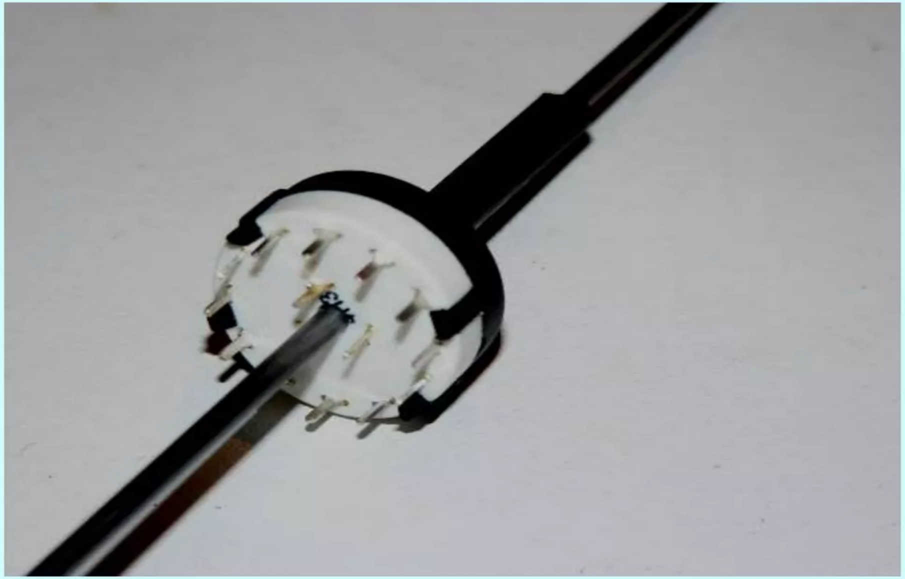
Characteristics:

- The surfaces are separated by a thick-film (at least 1000 Å thick) and hence there is no direct surface to surface contact.
- No welding of junctions.
- Since thick film lubricant covers/fills the irregularities on the both surfaces, there is no direct contact between material surfaces and so the wear is reduced.

In Fluid Film Lubrication, the Lubricating properties depend on:

- Viscosity of lubricant (Lubricant should be of low viscosity).
- Thickness of lubricant layer.
- Relative velocity and area of moving/sliding surfaces.

Example: Shaft running (Journal bearings)



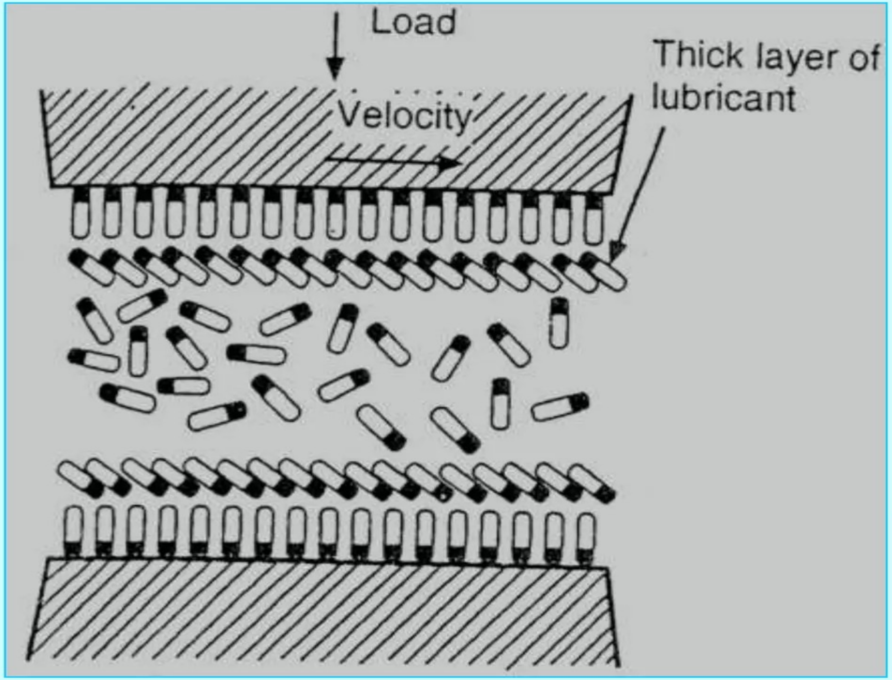
Lubricant oil covers the irregularities of the shaft as well as the bearing surfaces.

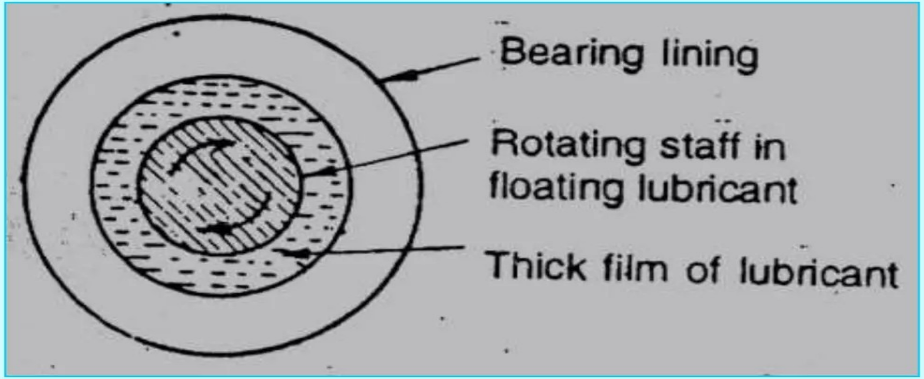
- Examples where fluid film lubrication is used are :
  - i) Sophisticated instruments
  - ii) Light machines like watches, guns, sewing machines etc.
- Examples for fluid-film lubricants are:

Hydrocarbon oils are considered to be satisfactory lubricants.

- ➢ To maintain viscosity throughout lifecycles long chain polymers are used as blenders with normal hydrocarbons oils.
- ➢ Small amount of unsaturated hydrocarbons present in hydrocarbon oils produced from petroleum fractions, which causes oxidation and produce gummy like products. Hence, anti-oxidant like aminophenol are used in journal bearings with lubricant

Mechanism of fluid film lubrication





2. Boundary Lubrication/Thin-film Lubrication

Characteristics of thin film lubrication are:

- High viscosity-index.
- Resistance to heat and oxidation.
- Good Oiliness.
- Low pour-point.

Mechanism of Boundary Lubrication/Thin-film Lubrication

This Lubrication takes place due to:

- Adsorption of lubricating oils to both surfaces by physical/chemical means.
- The adsorbed layers on the both metal surfaces carry the applied load.
- Co-efficient of friction, f = 0.05 - 0.15 and distance between surfaces is to be the order of the distance of the asperities.

For boundary lubrication, the lubricant molecule should have:

(i) Long hydrocarbon chain with polar groups.

(ii) Polar groups promote spreading and orientation
over the metallic surfaces at high pressure.

(iii) Lateral attraction between the chains.

(iv) Active groups or atoms, which can form chemical
linkages metal or other surfaces.

Examples of Boundary lubrication

- **Vegetable and animal oils (glycerides of higher fatty acids & their soaps).**
  - These oils either physically adsorbed to metal surfaces or react chemically at the metal surfaces.
  - Although these oils posses greater adhesion property, yet they tend to breakdown at high temperatures. Hence, fatty acids are added to improve the oiliness.
- **Graphite and Molybdenum disulphide alone or oil suspension may be used because:**
  - They have Low internal friction
  - They can bear/withstand compression
  - They are thermally stable

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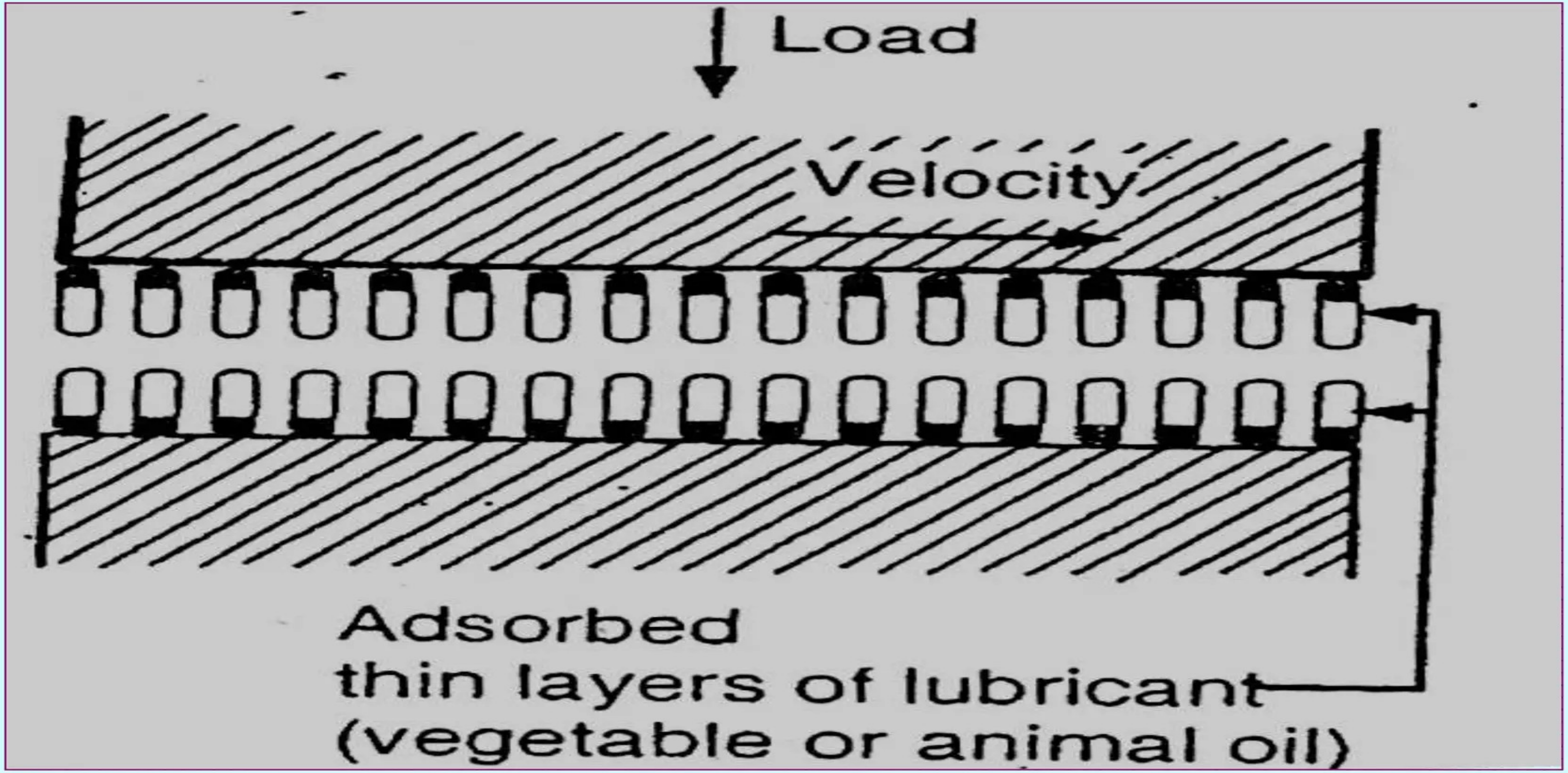
  - They are thermally stable

Mechanism of Boundary Lubrication



3. Extreme-pressure Lubrication

- **When moving/sliding surfaces are under very high pressure and speed, a high local temperature is attained.**
- **In such conditions, liquid lubricants fail to stick and may decompose and even vaporize.**
- **To avoid this, special additives are added to mineral oils. These are called "extreme-pressure additives".**

Mechanism

- **The "extreme-pressure additives" form on metal surfaces more durable films, capable of withstanding very high loads and high temperatures.**

Examples:

- **Organic compounds containing chlorine, sulphur and phosphorus.**

- **These compounds react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulphide or phosphides.**
- **These metallic compounds possess high melting points.**

CLASSIFICATION OF LUBRICANT

- Based on Physical state, lubricants are classified as:

a) Lubricating oils or liquid lubricants

b) Semi solid lubricants or greases

c) Solid lubricants

Types of Liquid Lubricants

a) Animal and Vegetable oils:

- Usable under very high temperature and heavy load.

❖ Disadvantages of its usages are

1. Costly
2. Undergo oxidation easily in contact with air and forms gummy and acidic products, and get thickened.
3. Tendency to hydrolyze in contact with moist-air or aqueous medium.

So, they are used as "*blending agents*" with other mineral oils.

b) Mineral oils or petroleum oils:

- They are obtained by distillation of petroleum.

- Length of hydrocarbon chain varies between 12 to 50 carbon atoms.
- Shorter- chain oils have lower viscosity than the longer- chain hydrocarbons.

- **Liquid lubricants are most widely used lubricants because they are**
  1. Cheap
  2. Available in abundance
  3. Quite stable under service conditions.

- But they have *poor oiliness character* compared to animal and vegetable oils.

- So, high molecular weight compounds like oleic acid, stearic acid are used to over come this problem.

c) Blended oils:

- No single oil serves as the most satisfactory lubricant for many of the modern machines. Hence, additives are used to improve the properties. These blended oils give desired lubricating property required for a machinery.

***Additives* used are:**

a) ***Oiliness- carriers:***

- Coconut oil, caster oil, and palmitic, stearic and oleic acids.

b) ***Extreme-Pressure additives such as:***

- Fatty esters or acids which form oxide film with metal surface.
- Organic materials containing sulphur.
- Organic chlorine compounds.
- Organic phosphorous compounds.
- Sometimes lead (Pb) compounds could be used as high pressure lubricants.

c) ***Pour-point depressing additives:***

- Phenol, condensation product of chlorinated wax with naphthalene.

d) *Viscosity index improvers* : hexanol

e) *Thickeners* : Polystyrene or polystyers

f) *Antioxidants or inhibitors* : Aromatic phenolic or amino compounds

g) *Corrosion preventers* : Phosphorous or Antimony organic compounds

h) *Abrasion inhibitors* : tricresyl phosphate

i) *Antifoaming agents* : glycols and glycerol

j) *Emulsifiers* : sodium salts of sulphonic acid

k) *Deposit inhibitors* : detergents such as salts of phenol and carboxylic acids

2. Semi-Solid Lubricants or Greases

- Semi solid consisting of a soap dispersed throughout a liquid lubricating oil.

- May be Petroleum oil or synthetic oil with a specific additive.

Preparation:

Saponification of fat (such as tallow or fatty acid) with alkali (like lime, caustic soda etc.,)

↓

Addition to hot lubricating oil under agitation

- To increase the heat resistance of grease, inorganic solid thickening agents (like finely divided clay, bentonite, colloidal silica, carbon block etc.,) are added.
- Have higher shear or frictional resistance than oils and hence support much heavier load at lower speeds.

Applications of Greases:

- When oil cannot remain in place due to high load, low speed, intermittent operation, sudden jerks etc.
- Work at high temperature
- When external contamination may create problem
- When dripping or spurting of oil is undesirable

Types of greases:

- Calcium based greases or cup-greases
- Soda-based greases
- Lithium-based greases
- Axle- greases → lime with resin and fatty acids
- Graphite greases
- Soap stone

3. SOLID LUBRICANTS

Solid lubricants are used when:

- Other lubricants can not be used
- Contamination undesirable
- Too high temperature or load are involved
- Combustible lubricants not acceptable

Examples of solid lubricants used are:

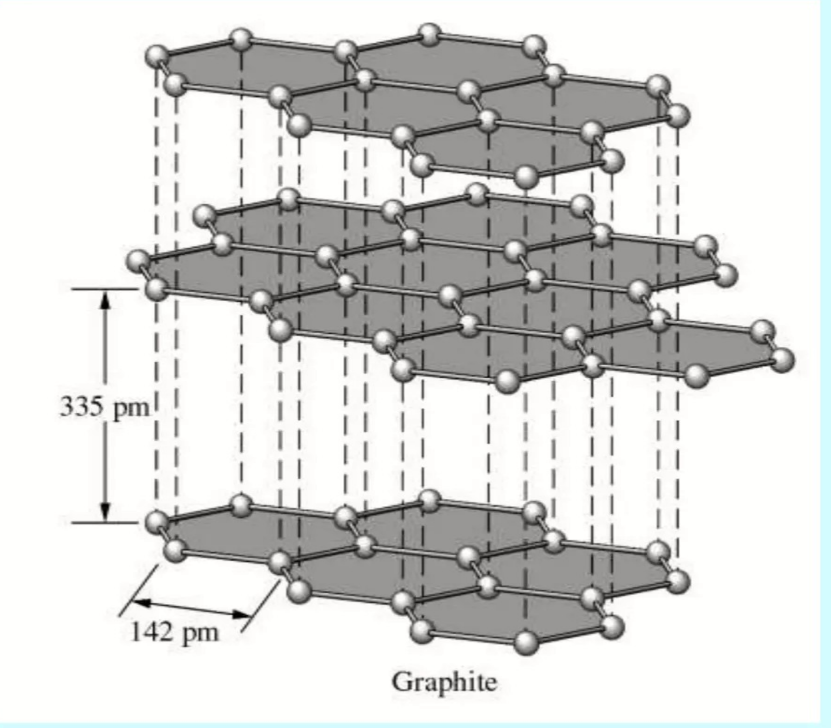
a) Graphite (or)

b) Molybdenum disulphide

Examples of Solid Lubricants

1.Graphite:

- Very soapy in touch
- Non inflammable
- Not oxidized in air below 375°C
- Oil + graphite → oildag
- Water + Graphite → aquadag
  - Emulsifying agent (tannin)
- Grease + graphite → graphite -greases

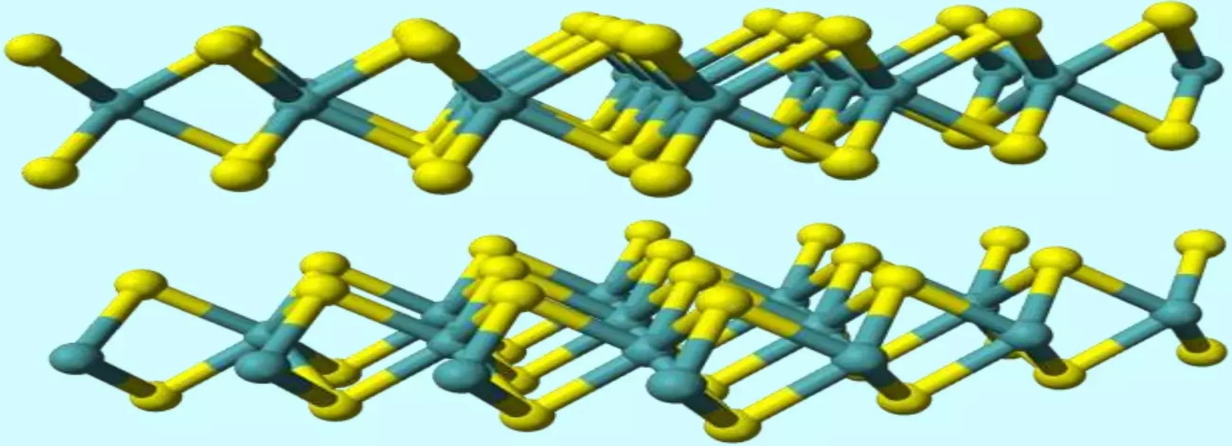


Graphite

Examples of Solid Lubricants

2. Molybdenum disulphide:

- Low coefficient of friction
- Stable in air up to 400 ° C



- Soapstone, talc or mica are also used as solid lubricants.