UNIT-1

WATER AND ITS TREATMENT

INTRODUCTION:

Water is nature's most wonderful, abundant and useful compound. Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. It is widely used in drinking, bathing, sanitary, washing, irrigation, fire-fights, air-conditioning and also production of industrial materials. The distribution of water on the Earth's surface is extremely uneven. Only 3% Of freshwater (69% resides in glaciers, 30% underground, and less than 1% is located in lakes, rivers and swamps.) of water on the surface is fresh; the remaining 97% resides in the ocean. Looked at another way, only one percent of the water on the Earth's surface is usable by humans, and 99% of the usable quantity is situated underground.

Types of Impurities present in water:

The natural water is usually contaminated by different types of impurities.

They are mainly three types.

- Physical impurities
- Chemical impurities
- Biological impurities

1. Physical impurities:

- *Colour:* in water is caused by metallic substances like salts.
- *Turbidity:* is due to the colloidal, extremely fine suspensions such as insoluble substances like clay, slit, and micro-organisms.
- *Taste:* presence of dissolved minerals in water produces taste. Bitter taste can be due to the presence of Fe, Al, Mn, Sulphates and lime. Soap taste can be due to the presence of large amount of sodium bicarbonate.
- *Odour:* In water is undesirable for domestic as well as industrial purpose.

2. Chemical impurities:

- *Inorganic chemicals:* Cations(Al^{+3}, Ca^{+2}, Mg^{+2}, Fe^{+2}, Zn^{+2}, Cu^{+2} Na^{+}, K^{+}), Anions(Cl^{-}, SO_4^{-2}, NO_3^{-}, HCO_3^{-}, F^{-}, NO_2^{-})
- *Organic chemicals:* dyes, paints, petroleum products, pesticides, detergents, drugs textile materials, other organic related materials.

3. Biological Impurities:

- Biological impurities are Algae, pathogenic bacteria, fungi, viruses, pathogens, parasite-worms.

HARDNESS OF WATER

Hardness of water defined as which prevent the lathering of soap. This is due to presence of certain salts like Ca^{+2}, Mg^{+2} and other heavy metals dissolved in water. Soaps (Sodium or Potassium salts of higher fatty acids) like Stearic acids ($C_{17}H_{35}COONa$).

Soft Water: The water which gives more lather with soap is called soft water.

$$\underset{\text{soap}}{C_{17}H_{35}COONa} + H_2O \rightarrow \underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + NaOH$$

Hard Water: The water which does not give lather with soap is called hard water. This is due to presence of certain salts like Ca^{+2}, Mg^{+2} and other heavy metals dissolved in water

$$\underset{\text{soap (soluble)}}{2C_{17}H_{35}COONa} + \underset{\text{salts (soluble)}}{CaCl_2/MgCl_2} \rightarrow \underset{\text{insoluble scum}}{(C_{17}H_{35}COO)_2\,Ca/Mg} + 2NaCl$$

CAUSES OF HARDNESS

Hardness of water is due to the presence of Bicarbonates, Chlorides, Sulphates and Nitrates of Calcium and Magnesium. These soluble salts get mixed with natural water due to the following reasons:

1. When natural water containing CO_2 flows over the rocks of the limestone ($CaCO_3$) and Dolamite ($CaCO_3$ & $MgCO_3$), they get converted into soluble bicarbonates. Thus, water gets hardness.

$$\underset{\text{Insoluble}}{CaCO_3} + H_2O + CO_2 \rightarrow \underset{\text{Soluble}}{Ca\,(HCO_3)_2}$$

2. When natural water flows over the rocks containing chlorides and sulphates and Nitrates of Calcium and magnesium, these salts dissolve in water. Thus water gets hardness.

DISADVANTAGES OF HARDNESS

1. In Domestic use:

- **Washing:** Hard water, when used for washing purposes, does not producing lather freely with soap. As a result cleaning quality of soap is decreased and a lot of it is wasted.
- **Bathing:** Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleaning quality of soap is depressed and a lot of it is wasted.
- **Cooking:** The boiling point of water is increased because of presence of salts. Hence more fuel and time are required for cooking.
- **Drinking:** Hard water causes bad effects on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

2. Industrial Use:

- **Textile Industry:** Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
- **Sugar Industry:** The water which containing sulphates, nitrates, alkali carbonates are used in sugar refining, cause difficulties in the crystallization of sugar.
- **Dyeing Industry:** The dissolved salts in hard water may reacts with costly dyes forming precipitates.
- **Paper Industry:** Calcium, magnesium, Iron salts in water may affect the quality of paper.
- **Pharmaceutical Industry:** Hard water may cause some undesirable products while preparation of pharmaceutical products.

3. Steam generation in Boilers:

- For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as: Scales & sludges formation, Corrosion, Priming & Foaming and Caustic embrittlement.

TYPES OF HARDNESS

Hardness of water is mainly two types:

1. Temporary Hardness 2. Permanent Hardness

1. Temporary Hardness: Temporary Hardness mainly caused by the presence of dissolved bicarbonates of Calcium, Magnesium ($Ca(HCO_3)_2$, $Mg(HCO_3)_2$). Temporary Hardness can be largely removed by boiling of water.

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{by heating}} CaCO_3\downarrow + H_2O + CO_2$$

$$\underset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\text{by heating}} Mg(OH)_2\downarrow + 2CO_2$$

2. Permanent Hardness: It is due to the presence of dissolved Chlorides, Nitrates and Sulphates of Calcium, Magnesium, Iron and other metals. Permanent hardness responsible salts are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$. Permanent Hardness cannot be removed by boiling but it can be removed by the use of ***chemical agents***.

EXPRESSION AND UNITS OF HARDNESS

The expression of hardness producing salts usually expressed in terms of an equivalent amount of $CaCO_3$. Calcium Carbonate is chosen as a standard because:

i. Its molecular weight (100) and equivalent weight (50) is a whole number, so the calculations in water analysis can be simplified.
ii. It is the most insoluble salt that can be precipitated in water treatment.

The conversion of the hardness causing salts into $CaCO_3$ equivalents can be achieved by using the following formula:

$$\text{Degree of Hardness} = \frac{\text{The weight of hardness causing salts}}{\text{Molecular weight of hardness causing salts}} \times 100\ (\text{Molecular weight of } CaCO_3)$$

Units of Hardness:

1. Parts per Million (ppm): The number of parts of calcium carbonate equivalent hardness presents in 10^6 parts of water.

1ppm = 1 part of $CaCO_3$ eq hardness in 10^6 parts of water.

2. Milligrams per litre (mg/l): The number of milligrams of calcium carbonate equivalent hardness presents in litre of water.

1 mg/L = 1 mg of $CaCO_3$ eq hardness in 1 litre of water.

But one litre of water weights =1 kg =1000g = 1000 x 1000 mg = 10^6 mg = 1 ppm.

3. Clark's degree (°Cl): The number of parts of calcium carbonate equivalent hardness presents in 70,000 or (7×10^4) parts of water.

1° Clarke = 1 part of $CaCO_3$ eq hardness per 70,000 parts of water.

4. Degree French (°Fr): The number of parts of calcium carbonate equivalent hardness presents in 10^5 parts of water.

1° Fr = 1 part of $CaCO_3$ hardness eq per 10^5 parts of water.

Relationship between various units of hardness:

1 ppm = 1 mg/L = 0.1° Fr = 0.07° Cl
1 mg/L = 1 ppm = 0.1° Fr = 0.07° Cl
1 ° Cl = 1.433° Fr = 14.3 ppm = 14.3 mg/L
1 ° Fr = 10 ppm = 10 mg/L = 0.7° Cl

Problem-1: A sample of water is found to contains following dissolving salts in milligrams per litre $Mg(HCO_3)_2$ = 73, $CaCl_2$ = 111, $Ca(HCO_3)_2$ = 81, $MgSO_4$ = 40 and $MgCl_2$ = 95. Calculate temporary and permanent hardness and total hardness.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	73	146	73×100/146 = 50
$CaCl_2$	111	111	111×100/111 = 100
$Ca(HCO_3)_2$	81	162	81×100/162 = 50
$MgSO_4$	40	120	40×100/120 = 33.3
$MgCl_2$	95	95	95×100/95 = 100

Temporary hardness = $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$
= 50 + 50 = 100mgs/Lit.

Permanent hardness = $CaCl_2$ + $MgSO_4$ + $MgCl_2$
= 100 + 33.3 + 100 = 233.3mgs/Lit.

Total hardness = Temporary hardness + Permanent hardness
= 100 + 233.3 = 333.3mgs/Lit.

Problem-2: A sample of water is found to contains following dissolving salts in milligrams per litre $Mg(HCO_3)_2$ = 16.8, $MgCl_2$ = 12.0, $MgSO_4$ = 29.6 and NaCl = 5.0. Calculate temporary and permanent hardness of water.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	16.8	146	16.8×100/146 = 11.50
$MgCl_2$	12.0	95	12.0×100/95 = 12.63
$MgSO_4$	29.6	120	29.6×100/120 = 24.66
NaCl	5.0	NaCl does not contribute any hardness to water hence it is ignored.	

Temporary hardness = $Mg(HCO_3)_2$ = 11.50mgs/Lit.

Permanent hardness = $MgCl_2 + MgSO_4$ = 12.63 + 24.66 = 37.29mgs/Lit.

Problem-3: A sample of water is found to contains following analytical data in milligrams per litre $Mg(HCO_3)_2$ = 14.6, $MgCl_2$ = 9.5, $MgSO_4$ = 6.0 and $Ca(HCO_3)_2$ = 16.2. Calculate temporary and permanent hardness of water in parts per million, Degree Clarke's and Degree French.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	14.6	146	14.6×100/146 = 10
$MgCl_2$	9.5	95	9.5×100/95 = 10
$MgSO_4$	6.0	120	6.0×100/120 = 5
$Ca(HCO_3)_2$	16.2	162	16.2×100/162 =10

Temporary hardness [$Mg(HCO_3)_2 + Ca(HCO_3)_2$] = 10 + 10 = 20mg/Lit
= 20ppm
= 20×0.07°Cl = 1.4°Cl
= 20×0.1°Fr = 2°Fr

Permanent hardness [$MgCl_2 + MgSO_4$] = 10 + 5 = 15mg/Lit
= 15ppm
= 15×0.07°Cl = 1.05°Cl
= 15×0.1°Fr = 1.5°Fr

Problem-4: Calculate the amount of temporary and permanent hardness of a water sample in Degree Clarke's, Degree French and Milligrams per Litre which contains following impurities.
$Ca(HCO_3)_2$ = 121.5 ppm, $Mg(HCO_3)_2$= 116.8 ppm, $MgCl_2$ = 79.6 ppm and $CaSO_4$ = 102 ppm.

Solution:

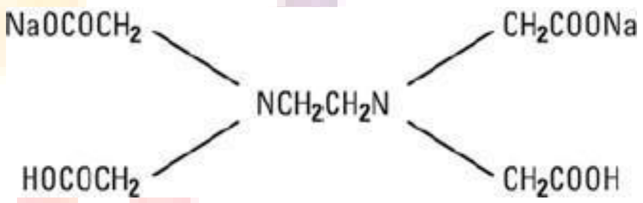
Name of the hardness causing salts	Amount of the hardness causing salts(ppm)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (ppm)
$Ca(HCO_3)_2$	121.5	162	121.5×100/162 = 75
$Mg(HCO_3)_2$	116.8	146	116.8×100/146 = 80
$MgCl_2$	79.6	95	79.6×100/95 = 3.37
$CaSO_4$	102	136	102×100/136 = 75

Temporary hardness [$Mg(HCO_3)_2 + Ca(HCO_3)_2$] = 75 + 80 = 155 ppm
= 155×0.07°Cl = 10.85°Cl
= 155×0.1°Fr = 15.5°Fr
= 155×1mg/Lit = 155 mg/Lit

Permanent hardness [$MgCl_2 + CaSO_4$] = 10 + 5 = 15mg/Lit
= 15ppm
= 15×0.07°Cl = 1.05°Cl
= 15×0.1°Fr = 1.5°Fr

DETERMINATION OF HARDNESS BY COMPLEXOMETRIC METHOD / EDTA METHOD

Principle: The determination of hardness is carried out by titrating water sample with Sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) using Eriochrome Black-T as an indicator and keeping the pH of the water at 9.0 - 10.0. The end point is the change in colour from wine - red to blue, when the EDTA solution complexes the calcium and magnesium salt completely.



$$\underset{\text{Hardness-salts}}{(Ca^{2+} \text{ or } Mg^{2+})} + \underset{\text{indicator}}{EBT} \rightarrow \underset{\text{unstable complex (wine red)}}{[Ca-EBT] \text{ (or) } [Mg-EBT]}$$

$$\underset{\text{Unstable complex (wine red)}}{[Ca-EBT] \text{ (or) } [Mg-EBT]} + EDTA \rightarrow \underset{\text{stable complex (colourless)}}{[Ca-EDTA] \text{ (or) } [Mg-EDTA]} + \underset{\text{blue}}{EBT}$$

Chemicals Required:

i. **Preparation of standard hard water (0.01M):** Dissolve 1g of pure, dry $CaCO_3$ in minimum quantity of dil.HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 Litre solution. Each ml of this solution thus contains 1mg of $CaCO_3$ equalent hardness.

ii. **Preparation of EDTA solution:** Dissolve 4 g of pure EDTA crystals + 0.lg $MgCl_2$ in 1 Litre of distilled water.

iii. **Preparation of Indicator (EBT):** Dissolve 0.5 g of Eriochrome Black−T in 100mL alcohol.

iv. **Preparation of Buffer solution:** Add 67.5g of NH_4Cl to 570 ml of Con. Ammonia solution and then dilute with distilled water to 1 Litre.

Various steps involved in this method:

1. **Standardization of EDTA solution:** Rinse and fill the burette with EDTA solution. Pipette out 20 ml of standard hard water (M_1) in a conical flask. Add 4ml of buffer solution and 2 drops of EBT

indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by **'X' ml**.

$$M_1 V_1 = M_2 V_2$$

Where, M_1 = Molarity of Standard Hard water (0.01M),
V_1 = Volume of Standard Hard water (20 ml),
M_2 = Molarity of EDTA,
V_2 = Volume of EDTA **(Xml)**.

2. **Determination of Total Hardness:** Rinse and fill the burette with EDTA solution. Pipette out 20 ml of sample water (V_3) in a conical flask. Add 4 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by **'Y' ml**.

$$M_2 V_2 = M_3 V_3$$

Where, M_2 = Molarity of EDTA,
V_2 = Volume of EDTA **(Yml)**.
M_3 = Molarity of sample water,
V_3 = Volume of Sample water (20 ml).

Total Hardness = $M_3 \times$ Molecular weight of $CaCO_3$ (100) × One Litre (1000ml)
= $M_3 \times 10^5$ ppm

3. **Determination of Permanent Hardness:** Take 100 ml of sample water in 250 ml beaker. Boil it to remove temporary hardness to about half of its volume and cool to room temperature, filter through filter paper to remove insoluble salts. Make up the volume to the original 100ml by adding distilled water. Now Pipette out 20 ml of this solution (V_4) in a conical flask. Add 4 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by **'Z' ml**.

$$M_2 V_2 = M_4 V_4$$

Where, M_2 = Molarity of EDTA,
V_2= Volume of EDTA (**Z ml)**.
M_4 = Molarity of Permanent hard water,
V_4 = Volume of Permanent hard water (20 ml)

Permanent Hardness = $M_4 \times$ Molecular weight of $CaCO_3$ (100) × One Litre (1000ml)
= $M_4 \times 10^5$ ppm

4. **Determination of Temporary Hardness:**

Temporary Hardness = Total Hardness - Permanent Hardness

Problem-1: 50 ml of standard hard water containing 1 gram of pure $CaCO_3$ per liter consumed 20 ml of EDTA. 50 ml of hard water consumed 25 ml of same EDTA solution EBT indicator. Calculate the total hardness of water sample in ppm.

Solution:

Strength of standard hard water sample ($CaCO_3$ solution) M_1=

$$\frac{\text{Weight of } CaCO_3}{\text{Mol. wt of } CaCO_3} \times \frac{1000}{1000}$$

$$= \frac{1 \text{ gm}}{100} \times \frac{1000}{1000} = 0.01 \text{ M}$$

Strength of EDTA solution M_2 $= \frac{V_1 M_1}{V_2} = \frac{50 \times 0.01}{20} = 0.025$ M

V_1 = Volume of standard hard water (50 ml), M_1 = Strength of standard hard water (0.01M)

V_2 = Volume of EDTA solution (20 ml), M_2 =Strength of EDTA solution =?

Calculation of Total hardness M_3 $= \frac{V_2 M_2}{V_3} = \frac{25 \times 0.025}{50} = 0.0125$ M

V_2 = Volume of EDTA solution (25 ml), M_2 =Strength of EDTA solution= 0.025M

V_3 = Volume of sample hard water (50 ml), M_3 = Strength of sample hard water =?

Total Hardness = 0.0125×10^5 ppm

= 0.0125×100 (Mol. Wt of $CaCO_3$) $\times 1000$ (ml)ppm

= 1250 ppm.

Problem-2: 0.28 grams of $CaCO_3$ were dissolved in HCl and the solution was made upto one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample consumed 33 ml of same EDTA solution EBT indicator. 100 ml of this water after boiling cooling and filtering required 10 ml of EDTA solution in titration. Calculate the permanent and temporary hardness of water sample in ppm.

Strength of standard hard water sample ($CaCO_3$ solution) M = $\frac{\text{Weight of } CaCO_3}{\text{Mol. wt of } CaCO_3} \times \frac{1000}{1000}$

$$= \frac{0.28\text{gm}}{100} \times \frac{1000}{1000} = 0.0028 \text{ M}$$

Strength of EDTA solution M_2 $= \frac{V_1 M_1}{V_2} = \frac{100 \times 0.0028}{28} = 0.01$ M

V_1 = Volume of standard hard water (100 ml), M_1 = Strength of standard hard water (0.0028M)

V_2 = Volume of EDTA solution (28 ml), M_2 = Strength of EDTA solution=?

Calculation of Total hardness M_3 $= \frac{V_2 M_2}{V_3} = \frac{33 \times 0.01}{100} = 0.0033$ M

V_2 = Volume of EDTA solution (33 ml), M_2 = Strength of EDTA solution (0.01M)

V_3 = Volume of sample hard water (100 ml), M_3 = Strength of sample hard water =?

Total Hardness = 0.0033×10^5 ppm = 0.0033×100 (Mol. Wt of $CaCO_3$) $\times 1000$ (ml)ppm

= 330 ppm

Calculation of Permanent hardness M_4 $= \frac{V_2 M_2}{V_4} = \frac{10 \times 0.01}{100} = 0.001$ M

V_2 = Volume of EDTA solution (10 ml), M_2 = Strength of EDTA solution (0.01M)
V_4 = Volume of sample hard water after boiling cooling and filtering (100 ml)
M_4 = Strength of sample hard water after boiling cooling and filtering =?

Permanent Hardness = 0.001×10^5 ppm
$= 0.001 \times 100$ (Mol. Wt of $CaCO_3$) $\times 1000$ (ml)ppm
$= 100$ ppm

Calculation of Temporary hardness = Total hardness - Permanent hardness
$= 330 - 100 = 230$ ppm

POTABLE WATER AND ITS SPECIFICATIONS

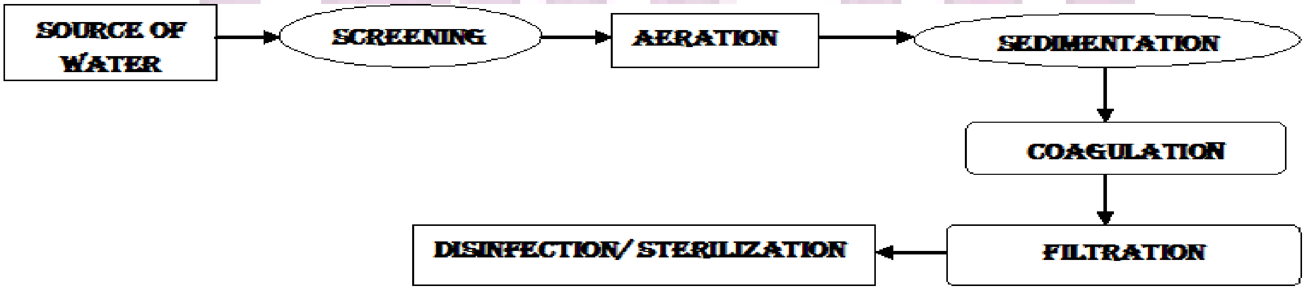
Water free from contaminants or water that is safe for human consumption is called potable water. The following are the **specifications of water drinking purpose.**

1. The water should be clear (colorless), odorless and pleasant taste.
2. The optimum *hardness* of water must be 125ppm.
3. The *pH* of potable water should be 7.0 to 8.0
4. The recommended maximum concentration of *total dissolved solids (TDS)* in potable water must not exceed 500 ppm.
5. The *turbidity* in drinking water should not exceed 10 ppm.
6. The water must be free from *heavy metals* like Lead, Arsenic, Chromium and Manganese.
7. The water must be *free from pathogenic bacteria*
8. The water must be *free from dissolved gases* like H_2S, CO_2 and NH_3.

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.,

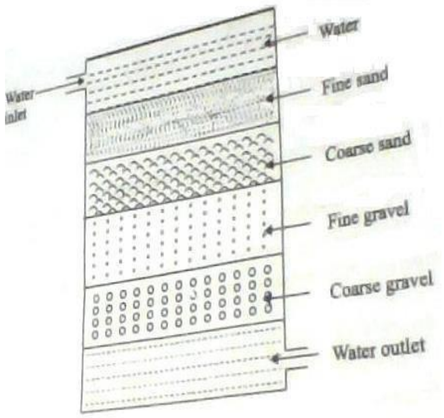


2. Coagulation:

3. 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.

4. 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.

5. The colloidal impurities are retained by the fine sand layer resulting the very slow filtration of water. Periodically the top layers of the fine sand layer is scraped off, washed, dried and introduced into the filter bed for reuse.



Sand filter

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

DISINFECTION OF POTABLE WATER

1. **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.

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

a. 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.

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

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

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

$$Cl_2 + NH_3 \rightarrow \underset{\text{Chloramine}}{ClNH_2} + HCl$$

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

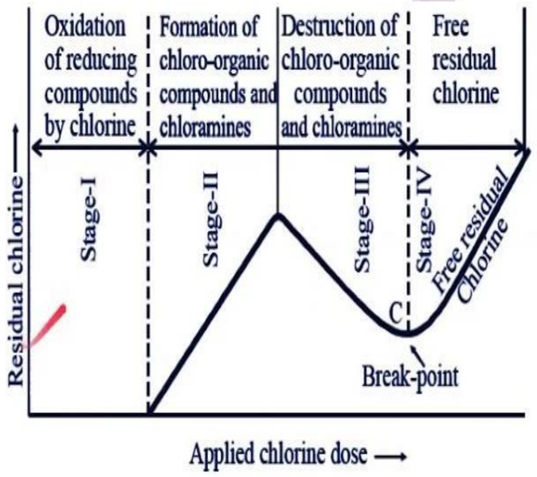
$$HOCl \rightarrow HCl + [O] \text{ nascent oxygen}$$

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 break-point chlorination.

The water sample is treated with chlorine and estimated for the residual chlorine in water and ploted 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 distruction 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**.

Advantages of break-point chlorination:

- It removes bad taste, colour, oxidizes completely organic compounds, ammonia and other reducingimpurities
- It destroys completely (100%) all disease producing bacteria.
- It prevents growth of any weeds in water.

DETERMINATION OF F^- ION BY ION- SELECTIVE ELECTRODE METHOD.

- An ion-selective electrode (ISE) is defined as an electro analytical sensor with a membrane whose potential indicates the activity of the ion to be determined (fluoride) in a solution.
- Ion-sensitive membrane may be glass, a crystalline inorganic material, or an organic ion exchanger.
- The membrane interacts with the ion of choice, here fluoride, allowing electrical potential of the half cell which is controlled by the fluorine concentration.

- The potential of the ISE is measured against a suitable reference electrode using a pH meter. The electrode potential is related to the logarithm of the concentration of the fluoride ion by the Nernst equation.

$$E = E^{0} + 2303\,\frac{RT}{nF}.\log\,[M]$$

n = ion charge, the equation is valid for very dilute solutions where the ionic strength is constant.

- In this experiment we will use fluoride-sensitive electrode, either a saturated calomel electrode or Ag/AgCl external reference electrode to measure the fluoride ion concentration.

- Flouride ISEs only respond to free ionized F^- in solution and can be used to measure this ion in the presence of other fluorine compounds.

Reagents required:

- NaF(dried at 100°C for 1 hour)
- KCl
- Liquid NaF unknown
- Flouride ISE and Ag/AgCl reference electrode
- pH meter capable of displaying mV potentials

Procedure:

- Dry the NaF solid for 1 hour at 100°C
- **NaF(10^{-1}):** Weigh 0.42 g of NaF, dissolve in deionized water, and dilute to 100 ml in a volumetric flask. This solution is about 10^{-1} F in NaF.
- Transfer 10 ml of above solution to 100 ml volumetric flask and dilute with deionized water. This solution is about 10^{-2} F in NaF.
- **KCl (1 M):** Weigh 7.55 g of KCl on a top loading balance and dissolve in 100 ml deionised water.
- Prepare four 100 ml volumetric standard flasks as follows:

NaF(10^{-2} M) ml	**KCl (1 M) ml**	Dilute each flask with deionised water
(a) 1.00	10	
(b) 2.00	10	
(c) 5.00	10	
(d)10.00	10	

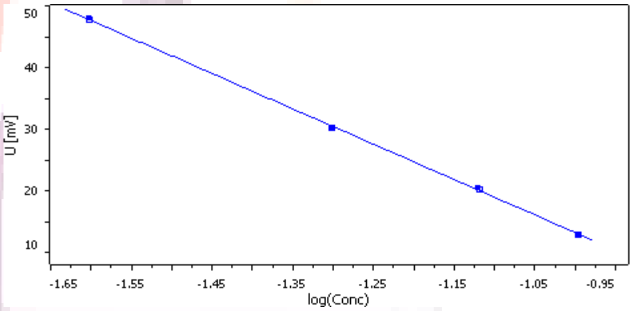
Analysis:

- Take unknown solution into a 100 ml volumetric flask and dilute upto the mark.
- Add 1 ml of prepared unknown solution and add 10 ml of KCl and dilute it to 100 ml with deionised water.
- Measure the potential in MV of the fluoride ISE Vs reference electrode for each of the four standard and for unknown solution.
- Pour about 30 ml of each standard solution (or) unknown into clean 100 ml beaker and immerse the electrode in the solution in the depth of 2 cm and then measure the electrode potential.

- After completion of the experiment rinse the electrodes with deionised water and keep the reference electrode in the appropriate solution.
- The F-ISE should be stored dry and loosely capped.

Calculations:

- Calculate the molarity of NaF accurately.



- Plot a graph of the concentration of NaF Vs potential. Find the best line passing through four standard solution points. Calculate the slope of the calibration curve slope = dE/dlog[NaF]
- By using calibration curve determine the concentration of NaF in your prepared unknown solution. Report this as percent fluoride (% w/v) in the prepared unknown.

BOILER TROUBLES

A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. The steam so generated is used in industries and generation of power. In modern pressure boilers and laboratories, the water required is used pure than the distilled water.

A boiler feed water should correspond with the following composition:

- Its hardness should be below 0.2ppm.
- Its caustic alkalinity (due to OH^-) should lie between 0.15ppm to 0.45ppm.
- It's should be free from dissolved gases like O_2, CO_2, in order to prevent boiler corrosion.

Excess of impurities in the boiler feed water generally cause the following problems:

1. Sludge's and Scale formation 2. Caustic embrittlement

Boilers are employed for the steam generation in power plants, where water as continuously heated to produce steam. As more and more water is removed from water in the form of steam, the boiler water gets concentrated with dissolved salts progressively reaches the saturation point. At this point the dissolved salts are precipitated out and slowly settle on the inner walls of the boiler plate. The precipitation takes place in two ways.

SLUDGES

Sludge is a soft, loosy and slimy precipitate formed within the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.

Ex: $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$.

Reasons for formation of sludges:

The dissolved salts whose solubility is more in hot water and less in cold water produce sludges.

Disadvantages of sludges:

1. Sludges are bad conductors of heat and results in the wastage of heat and fuel.
2. Excessive sludge formation leads to the settling of sludge in slow circulation areas such as pipe connections, plug openings, gauge–glass connections leading to the choking of the pipes.

Prevention of sludge formation:

a. By using soft water which is free from dissolved salts like $MgCO_3$, $MgCl_2$, $CaCl_2$ and $MgSO_4$ can be prevent sludge formation.

b. By blow down operation carried out frequently can prevent sludge formation.

(a) Sludge in boiler (b) Scale in boiler

Sludges and scales in boiler

SCALES

Scales are hard, adhering precipitates formed on the inner walls of the boilers. Scales are stick very firmly on to the inner walls of the boiler. It is removed with chisel and hammer. Scales are formed by decomposition of calcium bicarbonate in low pressure boilers.

Reasons for formation of scales:

a. **Decomposition of calcium bicarbonate:** The calcium bicarbonate at high temperature decomposes to calcium carbonate which is insoluble salt, forms scale in low pressure boilers.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

b. **Hydrolysis of Magnesium salts:** Magnesium salts gets hydrolyzed at high temperature forming $Mg(OH)_2$ precipitation which forms salt type scale.

$$MgCl_2 + H_2O \rightarrow Mg(OH)_2\downarrow + 2HCl$$

c. **Decomposition of calcium sulphate:** The solubility of $CaSO_4$ in water decreases with the increase in temperature and forms precipitation on the surface of the boiler further which forms hard scale. This type of scales is formed in high-pressure boilers.

d. **Presence of silica:** Sio_2 present even in small quantities, deposits as Calcium silicates ($CaSiO_3$) or Magnesium silicates ($MgSiO_3$). The deposits form hard scale and are very difficult to remove.

Disadvantages of Scales:

1. **Wastage of heat and fuels**: Scales poor thermal conductivity so that rate of heat transformation is reduced.

2. **Lowering of boiler safety** is due to overheating of the boiler material becomes softer and weaker, which causes distortion of boiler.

3. **Decrease in efficiency** of the boiler due to scales deposited in the values and condensers of the boiler cause choking.

4. **Danger of explosion** which happens the formation of the scales, the boiler plate faces higher temperature outside and lesser temperature inside due to uneven expansion. The water comes suddenly contact with overheated portion and larger amount steam is formed immediately, this results in development of sudden high pressure which may cause explosion of the boiler.

Prevention of scales:

a. If the scale formation is soft it can be removed by a scrapper, wire brush.

b. By giving thermal shocks, by sudden heating and sudden cooling which makes scale brittle and removed by scrubbing with wire brush.

c. If scale is very hard that is formed by $CaCO_3$ can be removed by washing with 5-10% HCl and $CaSO_4$ can be removed with EDTA solution.

CAUSTIC EMBRITTLEMENT

The formation of brittle and in crystalline cracks in the boiler shell is called caustic embrittlement.
The main reason for this is the presence of alkali-metal carbonates and bicarbonates in feed water. In lime-soda process, it is likely that, some residual Na_2CO_3 is still present in the softened water. This Na_2CO_3 decomposes to give NaOH and CO_2, due to which the boiler water becomes “Caustic Soda”.

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

The H_2O evaporates, the concentration of NaOH increase progressively creating a concentration cell as given below thus dissolving the iron of the boiler as sodium ferrate (Na_2FeO_2).

(-)Anode: ‘Fe’ at bents | Conc.NaOH ‖ Dil.NaOH | ‘Fe’ at plane Surface: Cathode (+)

This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail. The iron at plane surfaces surrounded by dilute NaOH becomes cathodic while the iron at bends and joints surrounded by highly concentrated NaOH becomes anodic which consequently decayed or corroded.

Caustic embrittlement can be prevented:

a. By maintaining the pH value of water and neutralization of alkali.

b. By using Sodium Phosphate as softening reagents, in the external treatment of boilers.

c. Caustic embrittlement can also be prevented by adding Tannin or Lignin or Sodium sulphate which prevents the infiltration of caustic-soda solution blocking the hair-cracks.

INTERNAL TREATMENT OF WATER

Principal: In this process an ion is prohibited to exhibit its original character by converting it intoother more soluble salt. Suitable chemicals are added to the boiler water either: a) to precipitate the scale forming impurities in the form of sludges or b) to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm. Internal treatment can be done following types.

1. Calgon conditioning: Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.
Calgon = Sodium hexa meta phosphate = $Na_2 [Na_4 (PO_3)_6]$

$$Na_2 [Na_4 (PO_3)_6] \rightarrow 2Na^+ + [Na_4P_6O_{18}]^{-2}$$

$$2CaSO_4 + [Na_4P_6O_{18}]^{-2} \rightarrow [Ca_2 P_6O_{18}]^{-2} + 2Na_2SO_4$$

2. 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.

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

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

Genarally three types of Phosphates are employed.

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

ii. Di sodium Phosphate ($Na_2 HPO_4$): 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.

3. Colloidal conditioning: The addition of organic substances such as Kerosene, tannin, agar-agar 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.

ION EXCHANGE PROCESS/DE MINERALISATION/DE IONISATION

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:

i. Cation Exchange Resins ii. Anion Exchange Resins.

i. **Cation Exchange Resins:** Cation exchange resins are styrene divinyl benzene co-polymers, which on sulphonation (or) carboxylation, which contains –COOH, $–SO_3H$ functional groups which responsible for exchanging their hydrogen ions with cations in water.

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

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

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

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

$$2RH + MgSO_4 \rightarrow R_2Mg + H_2SO_4$$

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

ii. **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.

$$ROH + HCl \rightarrow RCl + H_2O$$

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

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

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.

$$H^+ + OH^- \rightarrow H_2O$$

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

$$H^+ + OH^- \rightarrow H_2O$$

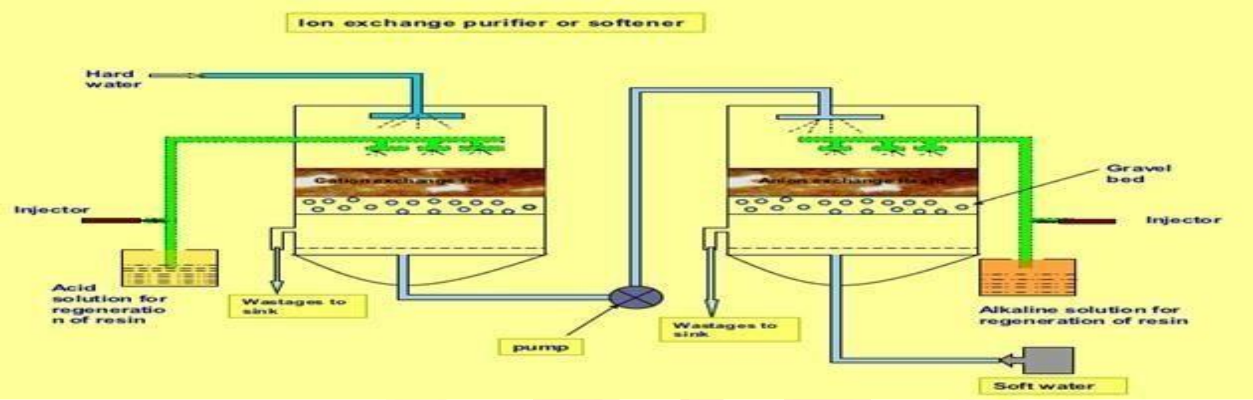
The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

Regeneration: When cation exchanger losses capacity of producing H^+ ions and exchanger losses capacity of producing OH^- ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.

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

$$R_2Mg + 2H_2SO_4 \rightarrow 2RH + MgSO_4$$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.



$R_2SO_4 + NaOH \rightarrow 2ROH + Na_2SO_4$

$$RCl + NaOH \rightarrow ROH + NaCl$$

$$RHCO_3 + NaOH \rightarrow ROH + NaHCO_3$$

Merits of Ion-exchange process:

- The process can be used to soften highly acidic or alkaline water.
- It produces water of very low hardness (2ppm)
- So it is very good for treating water for use in high-pressure boilers.

Demerits of Ion-exchange process:

- The equipment is costly and more expensive chemicals are needed.
- If water contains turbidity, the output of the process is reduced. The turbidity must be below 10ppm; else it has to be removed by coagulation and filtration.

DESALINATION OF WATER -REVERSE OSMOSIS

The process of removing common salt (Sodium Chloride) from the water is known as **desalination.**

The water containing dissolved salts with a salty or brackish taste is called **brackish water**.
Depending upon the quantity of dissolved solids, water is graded as:

i. Fresh Water: Contains less than 1000 ppm of dissolved solids.
ii. Brackish Water: Contains more than 1000 ppm to less than 35000 ppm of dissolved solids.
iii. Sea Water: Contains more than 35000 ppm of dissolved solids.

Sea water and brackish water can be made available as drinking water through desalination process. Desalination is carried out either by reverse osmosis or electro dialysis.

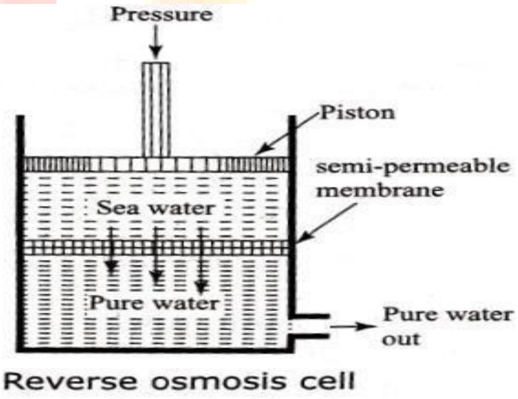
Reverse Osmosis:

Reverse Osmosis is a process in which pressure greater than the osmotic pressure is applied on the high concentration side of the membrane, the flow of solvent move from concentrated side to dilute side across the membrane.

Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane.

Method:

In this process pure water is separated from salt water. 15-40 kg/cm^2 pressure is applied for separating the water from its contaminants. The membranes used are cellulose acetate, polymethyl acrylate and polyamide polymers. The process is also known as **super or hyper filtration**.



Reverse osmosis cell

Advantages:

- It is simple and reliable process & Capital and operating expenses are low.
- The life of the semi-permeable membrane is about two years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.
- It removes colloidal silica which is not removed by demineralization.
- It removes ionic and non ionic impurities

UNIT-II

BATTERY CHEMISTRY

Galvanic cell: Galvanic cell is a device for converting chemical energy into electrical energy through spontaneous redox reaction.
Battery: It is a device consisting of two or more galvanic cells connected in series or parallel or both,which converts chemical energy into electrical energy through redox reaction.
Principle components of a battery are:
1. An anode where oxidation occurs.
2. A cathode where reduction occurs.
3. An electrolyte, which conducts ions.
4. A separator to separate anode and cathode compartments.

Classification of the Battery:
1. Primary Batteries: A battery which cannot be recharged(because the cell reactions are irreversible) e.g. Zn-MnO2,Zn –Air , dry cell.

2. Secondary Battery: A battery which can be recharged(as the cell reactions are reversible) and also known as storage battery. e.g. Lead-acid battery, Li-ion battery

3. Reserve battery: In this battery, one of the components is stored separately and used whenever required.
e.g. Mg-AgCl battery where battery is activated by the addition of water. It is used in missiles and military weapon system.

Lithium-ion battery:
Construction: Anode-Lithium interrelated graphite.
Cathode – Lithium metal oxide such as (LiCoO2).
Electrolyte -A solution of lithium salt (LiPF6) in organic solvent. Separator- non-woven polypropylene.
Representation : Li, C | LiPF6 , in organic solvent | LiCoO2 □

It is a rechargeable battery. In this battery lithium atoms occupy positions between graphite lattice layers. □ Lithium ions move between anode and cathode during discharging and charging process. Since both anode and cathodes are intercalation materials lithium atoms insert and disinsert between layers.

Working At Anode: LixC6 xLi+ + xe- + 6C
At cathode: Li1-xCoO2 + xLi+ + xe- LiCoO2
Net Cell reaction : Li1-xCoO2 + LixC6 6C + LiCoO2
Applications: Portable electronics, mobile phones, laptop, ipod etc.

Advantages of Li-ion Battery as an electrochemical storage system for electric vehicles: □
Eco-friendly: They have relatively low levels of toxic heavy metals such as Cd, Pb, Hg etc compared to other types of batteries such as Lead-acid and Ni-Cd batteries. □
Cell voltage : Li-ion Battery has cell voltage of 3.7 V which is high compared to other batteries like Ni-MH(1.2 V) □
Light weight and compact: Electrodes commonly used in Lithium ion batteries, Lithium and carbon, are light weight on their own and this makes them light weight and compact compared to other batteries. □

High energy density: Li element has the ability to release and store large amounts of energy. This allows li-ion batteries to pack high energy in small size. Because of high energy efficiency Li- ion batteries last much longer between charges than other rechargeable batteries – a parameter which is very important for electric car batteries. Performance at high temperatures is also good.

- Low maintenance: Ni-Cd or Ni-MH batteries have “memory effect” or “lazy battery effect” which causes them to hold less charge. They should be maintained by completely discharging or recharging them. Li-ion batteries don‟t suffer from memory effect and they give up their last bit of power. Hence maintenance is less.

- Low self-discharge rate: Self discharge rate of Li-ion batteries increases about 5% within first 24 hrs after charging and then tapers off to 1-2% per month.

- More charge cycles: Quality Li-ion batteries last about 1000 full charge

CORROSION AND ITS CONTROL

Corrosion can be defined as the loss of materials as a result of chemical or electrochemical reaction with the environment. The annual cost of corrosion in India is around Rs. 600 crores. The loss due to corrosion include the cost of repair or replacement of the corroded component or equipments. By making proper use of existing corroded materials and techniques for corrosion prevention, about 25% of the estimated amount (Rs. 150 crores in India) can be saved.

Now a days it is necessary to pay more attention to corrosion because of increasing use of metals in all fields of technology and increase in air and water pollution there by resulting in a more corrosive environment.

Definition :

Metals combines with oxygen gives metal oxide is called corrosion.

Destruction of metals (or) deterioration of metals by the attack of environment is called corrosion.

Causes of corrosion

Metals occur in nature are in the following two forms :

1. Native state

The metals occur in native (or) free (or) uncombined state are non-reactive with the environment. They are noble metals exist as such in the earth crust they have very good corrosion resistance.

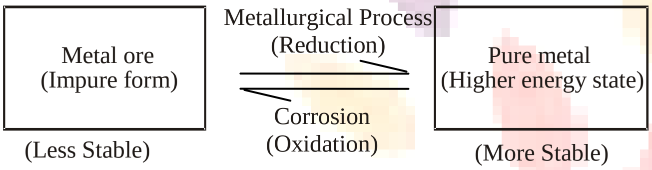
Example : Au, Pt, Ag, etc.,

2. Combined State

Except noble metals, all other metals are reactive and react with environment and form stable compounds, as their oxides, sulphides, chlorides, and carbonates. They exist in their form of stable compounds called ores and minerals.

Example : Fe2O3, ZnO, PbS, CaCO3, etc.,

The metal ores are converted into pure metal by the use of metallurgical process. The pure metal at higher energy will always have a tendency to go into the lower energy state by the attack of environment is called corrosion.



3.2 CLASSIFICATION OF CORROSION

The corrosion process is classified on the basis of mechanisms.

(i) Dry corrosion (or) Chemical corrosion

(ii) Wet corrosion (or) Electro chemical corrosion

3.2.1 Dry Corrosion (or) Chemical Corrosion

This type of corrosion occurs through direct chemical action of dry gases (or) corrodents such as oxygen, halogen, H2S, SO2, etc.,

This can be classified as follows,

(1) Corrosion by oxygen (Oxidation corrosion)

Oxygen present in the atmosphere attacks metal surface resulting in the formation of metal oxide which is known as corrosion product and this process is known as oxidation corrosion.

Mechanism

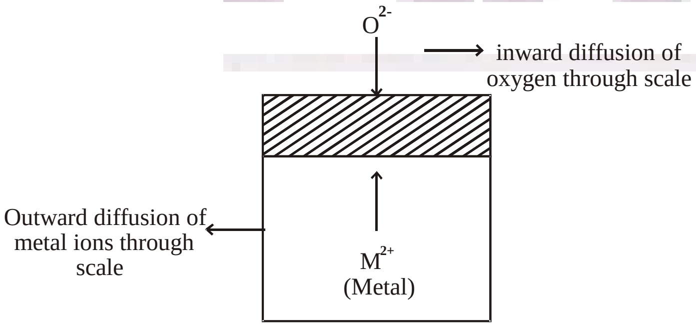


Fig : 3.1 Oxidation corrosion

Oxidation first occurs at the surface of the metal resulting in the formation of metal ions (M2+)

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

Oxygen is converted to oxygen ion (O2-)

$½O_2 + 2e^{-} \rightarrow O^{2-}$ (Reduction)

Metal ions combines with oxygen ions forms the metal oxide film

$M + ½O_2 \rightarrow M^{2+} + O^{2-} \rightarrow MO$ (Metal Oxide)

Nature of the metal oxide films formed

There are generally four types of metal oxide films are formed.

(i) Stable film

If the oxide film is stable, there is no further penetration of oxygen ions to the metal part. There is no further corrosion takes place. Thus the stable film act as protective coating.

Examples : Al, Sn, Pb, Cu, etc.,

(ii) Unstable film

In the case of noble metals the metal oxides formed decomposes reversibly to the metal and oxygen.

Metal oxide $\rightleftharpoons$ Metal + Oxygen

In this case, the corrosion is a continuous process.
Examples :
Pt, Ag, Au, etc.,

(iii) Porous film

The oxide layer formed in some cases are porous. In this case atmospheric oxygen can easily move to the metal surface.

So corrosion is a continuous process.
Examples :
Li, Na, K, etc.,

(iv) Volatile film

The oxide layer formed in some cases are volatile. So the oxide film volatises as soon as they are formed. The fresh metal surface is kept exposed all the time for further attack. Thus it act as a non-protective coating.

Example :
Molybdenum oxide film.

Pilling - Bed Worth rule

An oxide layer is protective (or) non-porous, the volume of the metal oxide formed is greater than the volume of the metal.

An oxide layer is non-protective (or) porous, the volume of the metal oxide formed is less than the volume of the metal.

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Li, Na, K, etc.,

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Molybdenum oxide film.

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An oxide layer is protective (or) non-porous, the volume of the metal oxide formed is greater than the volume of the metal.

An oxide layer is non-protective (or) porous, the volume of the metal oxide formed is less than the volume of the metal.

Protective layer metals e.g., Al, Sn, Pb, Cu, etc,.

Non protective metals e.g., Li, Na, K, Mg, Ca, Sr, etc,.

b) Corrosion by other gases

Other gases present in the atmosphere like SO2, CO2, Cl2, H2S etc,. can also attack the metals.

For example,

1. Chlorine attacks on silver forms protective layer of silver chloride, it prevents further corrosion.

$Cl_2 + 2Ag \rightarrow 2AgCl$

2.But Sn reacts with chlorine present in the atmosphere forms SnCl2.It is volatile. So the corrosion is a continuous process.

$Cl_2 + Sn \rightarrow SnCl_2$

3.Metals combines with H2S gas to liberate atomic hydrogen.

$H_2S + Fe \rightarrow FeS + 2H$ (atomic hydrogen)

The atomic hydrogen is very reactive and penetrate the metal and occupies the voids of the metal.

The atomic hydrogen recombines inside the metal and develop pressure which leads to cracking of the metal. This is known as “Hydrogen Embrittlement”.

4.Atomic hydrogen are formed by dissociation of H2 gas at high temperature.

$H_2 \rightarrow H + H$

5. The atomic hydrogen is highly reactive and combine with carbon present in the metal forms CH4 gas which leads to cracking of the metal surface. This is known as “Decarburisation”.

c) Liquid metal corrosion

This type of corrosion is due to the chemical action of flowing liquid metals at high temperature on solid metal.

Such type of corrosion are found in nuclear power plants.

3.2.2 Wet Corrosion (or) Electrochemical Corrosion

This type of corrosion occurs when,
(i) The conducting electrolytic liquid is in contact with metal.
(ii) Two dissimilar metals are partially dipped in the electrolyte.

In the above condition one part of the metal becomes anode and the remaining part becomes cathode.

In anodic area

Oxidation takes place with the liberation of electrons.

$$M \rightarrow M^{2+} + 2e^-$$

In cathodic area

Depending upon the nature of electrolytic solution, two types of reaction takes place at cathode.

(i) Hydrogen evolution mechanism
(ii) Oxygen Absorption mechanism

This can be explained as follows,

(i) Hydrogen evolution mechanism

When the conduction medium is highly acidic or completely free from dissolved oxygen, hydrogen evolution takes place. For example, corrosion of iron metal by industrial waste containing H+ ion undergoes this type of corrosion.

In this type of corrosion, anodes possess large surface area and less cathode area.

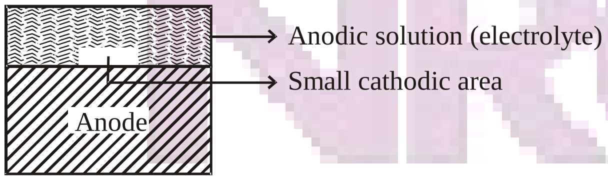


Fig : 3.2 Hydrogen Evolution

At anode : $Fe \rightarrow Fe^{2+} + 2e^-$ (Oxidation)
At cathode : $2H^+ + 2e^- \rightarrow H_2\uparrow$ (Reduction)
Overall : $Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$

(ii) Oxygen Absorption mechanism

This type of mechanism takes place when base metals are in contact with neutral solution like H2O with dissolved oxygen. An example of this kind of corrosion is the rusting of paint coated iron. If there is any crack in the paint coated iron, that area acts as anode.

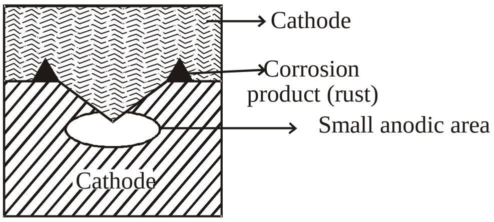


Fig : 3.3 Oxygen Absorption

The liberated electrons flows from the anode to the cathode through the metal and accepted along the electrolyte and oxygen at cathode.

At anode : $Fe \longrightarrow Fe^{2+} + 2e^{-}$ (Oxidation)
At cathode : $\frac{1}{2}O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-}$ (Reduction)
Overall : $Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^{-} \longrightarrow Fe(OH)_2$ (corrosion product)

If enough oxygen is present, ferrous hydroxide is converted into ferric hydroxide.

$4Fe(OH)_2 + O_2 + H_2O \longrightarrow 4Fe(OH)_3$ (Rust)

Table 3.1 Differences Between Chemical and Electro Chemical Corrosion

Sl. No	Dry (or) Chemical Corrosion	Wet(or)Electro Chemical Corrosion
1.	It occurs in dry state	It occurs in presence of moisture (or) electrolyte
2.	It follows adsorption mechanism	It follows the mechanism of electro chemical reaction.
3.	Corrosion product accumulate on the same spot, where corrosion occurs.	Corrosion occurs at anode while products gather at cathode
4.	Uniform corrosion behaviour is seen, i.e., either the whole surface of the metal in contact with the medium corrodes, or it does not.	Localised corrosion occurs. i.e., one metal surface alone is corroding even though both metal surfaces are in contact with the medium.
5.	Only heat evolution can be observed.	Due to electron flow from the site of oxidation to site of reduction, current flow can be observed.

3.2.3 Galvanic Corrosion

This type of electrochemical corrosion takes place when two dissimilar metals are joined in the presence of electrolyte. The metal with higher negative electrode potential acts as anode and the remaining parts acts as cathode.

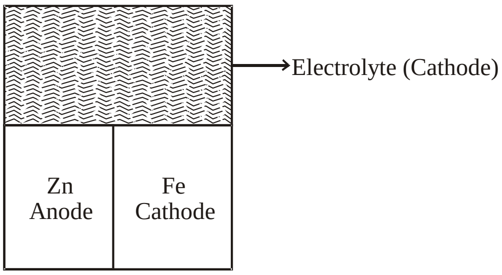


Fig : 3.4 Galvanic corrosion (Zn / Fe)

At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation)
At cathode : $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (Reduction)
Overall : $Zn + \frac{1}{2}O_2 + H_2O \longrightarrow Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$

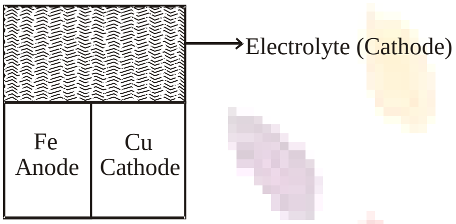


Fig : 3.5 Galvanic corrosion (Fe / Cu)

At anode : $Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)
At cathode : $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$
Overall : $Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$

The galvanic corrosion can be avoided by

1. Coupling of metals very close in the emf series.
2. Providing an insulating material between the two metals.
3. The area of the cathode is always smaller than anodic area.

3.2.4 Concentration Cell Corrosion (or) Differential Aeration Corrosion

This is the most common type of electrochemical corrosion that takes place when the metal is partially dipped in solutions, metals partially covered with dust, sand, water drops etc. The less aerated part act as anode and the more aerated part act as cathode. The anodic part undergo corrosion and the cathodic part is prevented. This type of corrosion called as Concentration Cell Corrosion.

Example : 1

When a metal is partially immersed in a solution it has very poor aeration when compared with the metal that is outside the solution.

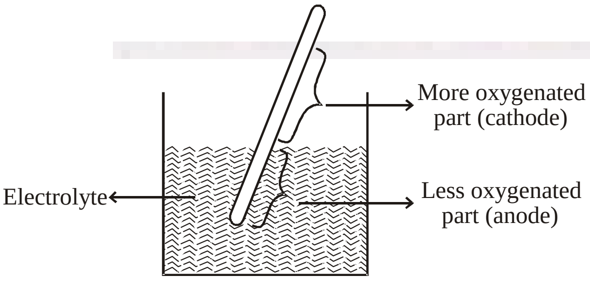


Fig. : 3.6 Concentration cell corrosion (Metal / Electrolyte)

The less aerated part act as anode and the more aerated part act as cathode.

Example: 2

The another example of this type of corrosion is the metal parts partially covered with dust, sand, water drops etc. This type of corrosion is called as pitting corrosion.

Pitting Corrosion

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

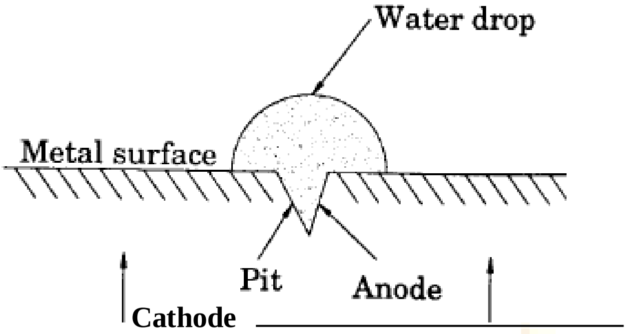


Fig Pitting Corrosion

The area covered by the drop of water act as an anode due to less oxygen concentration and suffers corrosion. The uncovered area (freely exposed to air) act as a cathode due to high oxygen concentration.

The rate of corrosion will be more, when the area of cathode is larger and the area of anode is smaller.

At anode : $Fe \longrightarrow Fe^{2+} + 2e^{-}$ (Oxidation)
At cathode : $\frac{1}{2}O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-}$
Overall

$$Fe + \frac{1}{2} O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^{-} \longrightarrow Fe(OH)_2 \xrightarrow{[O]} Fe(OH)_3$$

This type of intense corrosion is called pitting.

Corrosion is a kind of reaction that takes place in the metal by the influence of its environment. Hence both (i) the nature of the metal & (ii) the nature of environment play equal part in the corrosion of the metal. The following are the factors responsible for the corrosion.

I. Nature of the Metal

(a) Position of metal in the EMF series

Metals higher (-) in the galvanic series undergo strong corrosion and lower (+) in the EMF series undergo less corrosion.

(b) Relative areas of anode and cathode

Corrosion will be severe if the anodic area is small and the cathodic area is large. Larger cathodic area of the cathode will create demand of more electrons, which can be met by the smaller area of the anode only by undergoing more corrosion.

(c) Over potential

Corrosion is very slow if hydrogen over voltage of the cathodic metal is high. The over potential of a metal in a corrosive environment is inversely proportional to corrosion rate.

(d) Nature of the surface film

Stable oxide film restricts further corrosion. Unstable, volatile and porous oxide films enhances further corrosion.

(e) Purity of the metal

Impurity present in pure metal creates heterogenity and leads to galvanic corrosion. If the percentage of purity increases the corrosion rate decreases.

(f) Stress

Metals part under stress can become anode and undergo corrosion. This type of corrosion is called stress corrosion.

II. Nature of the Environment

(a) Temperature

Increase of temperature increases diffusion of ions in the corrosive medium and thus rises the corrosion rate.

(b) Humidity

Concentration of water vapour present in the atmosphere is known as humidity. If the humidity increases the corrosion rate increases, at a particular point a sudden increase in the corrosion rate is observed, that is called critical humidity.

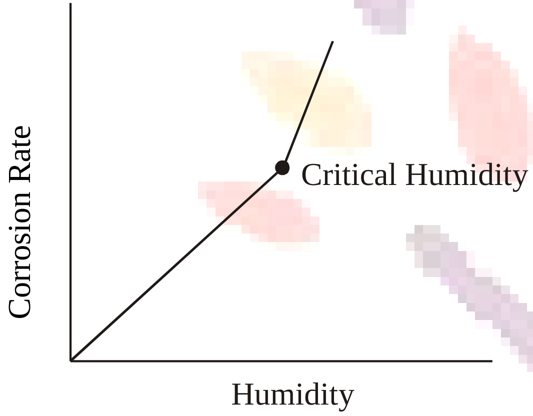


Fig. : 3.10 Critical Humidity

(c) Presence of Corrosive gases

Corrosive gases like So2, H2S, fumes of HNO3, H2SO4, acetic acid etc, enhances the corrosion rate.

(d) Presence of suspended solids

Suspended particles like chemically active, chemically inactive and chemically neutral dust particles enhances the corrosion rate.

(e) pH

The corrosion rate is maximum when the environment is more acidic (pH=5) and minimum when the environment is more alkaline (pH=11). In general, acidic medium is more corrosive than alkaline or neutral medium.

3.5 CORROSION CONTROL METHODS

The corrosion is controlled by the following methods.

(i) Sacrificial anodic protection
(ii) Impressed current cathodic protection
iii) Control of corrosion by modifying the metal
(iv) Corrosion Inhibitors.

3.5.1 Sacrificial Anodic Protection Method

In this method, the metallic structure to be protected is made cathode by connecting it with more active metal (anode metal). So that all the corrosion will concentrate only on the active metal. The artificially made anode thus gradually corroded protecting the original metallic structure. Hence, this process is otherwise known as sacrifical anodic protection.

Aluminium, Zinc, Magnesium are used as sacrificial anodes.

This method is used for the protection of ships and boats. Sheets of Mg or Zn are hung around the hull of the ship. (Fig. 3.11).

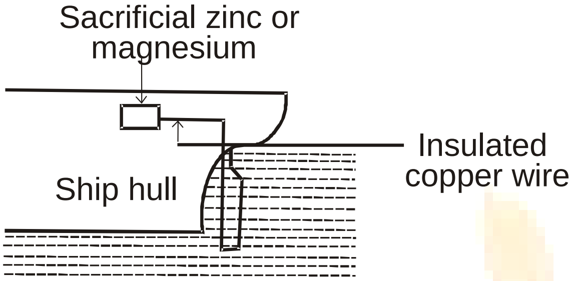
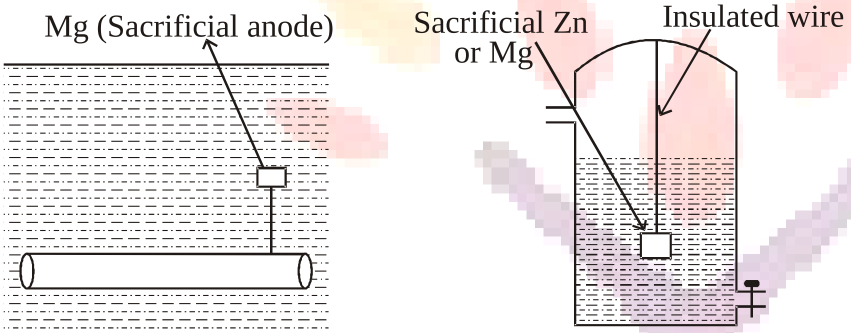


Fig. 3.11 Sacrificial anodic protection of ship

Zn or Mg will act as anode compared to iron (ship or boat is made of iron), so corrosion concentrates on Zn or Mg. Since they are sacrificed in the process of saving iron, they are called sacrificial anodes.



(a) Underground pipeline

(b) Boiler

Fig. 3.12 Sacrificial anodic protection

Important applications of sacrificial anodic protection are

a. Protection of underground pipelines, cables from soil corrosion (Fig. 3.12(a)).
b. Insertion of Mg sheets into the domestic water boilers to prevent the formation of rust (Fig. 3.12(b)).
c. Calcium metal is employed to minimize engine corrosion.

3.5.2 Impressed Current Cathodic Protection Method

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

This can be done by connecting negative terminal of the battery to the metallic structure to be protected, and positive terminal of the battery is connected to an inert anode. Inert anodes used for this purpose are graphite, platinised titanium. The anode is burried in a “back fill” (containing mixture of gypsum, coke, breeze, sodium sulphate). The “back fill” provides good electrical contact to anode (Fig. 3. 13).

Important applications of impressed current cathodic protection are structures like tanks, pipelines, transmission line towers, marine piers and laid-up strips, etc.

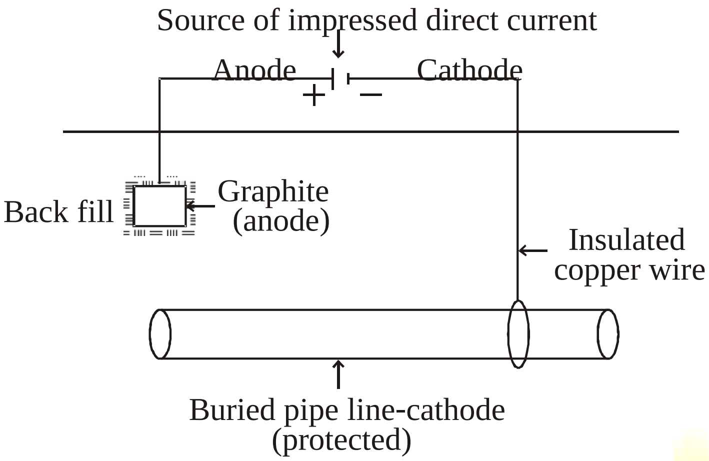


Fig. 3.13 Impressed current cathodic protection

This type of protection is given to underground water pipe lines, oil pipe lines, ships, etc.

Table 3.2 Comparison of Galvanic method (Sacrificial anode) and Impressed current cathodic method

Sl. No	Sacrificial anode method	Impressed current method
1.	No external power supply is necessary.	External power supply must be present.
2.	This method requires periodical replacement of sacrificial anode.	Here anodes are stable and do not disintegrate.
3.	Investment is low.	Investment is more.
4.	Soil and microbiological corrosion effects are not taken into account.	Soil and microbiological corrosion, corrosion effects are taken into account.
5.	This is most economical method especially when short-term protection is required.	This method is well suited for large structure and long term operations.
6.	This method is suitable when the current requirement and the resistivity of the electrolytes are relatively low.	But this method can be practiced even if the current requirement and the resistivity of the electrolyte are high.

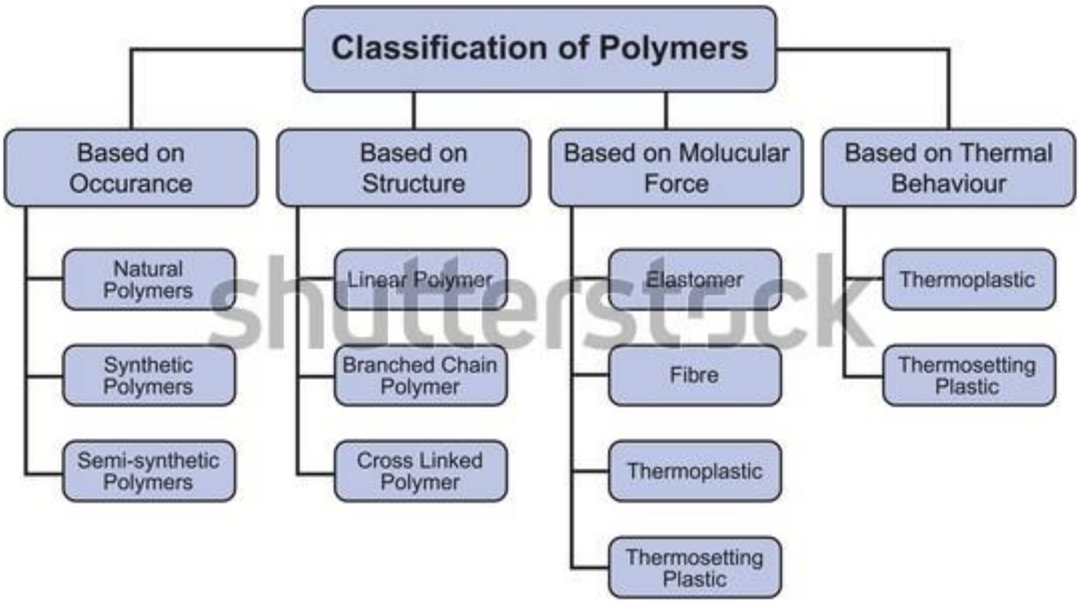
UNIT IV
POLYMERIC MATERIALS

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



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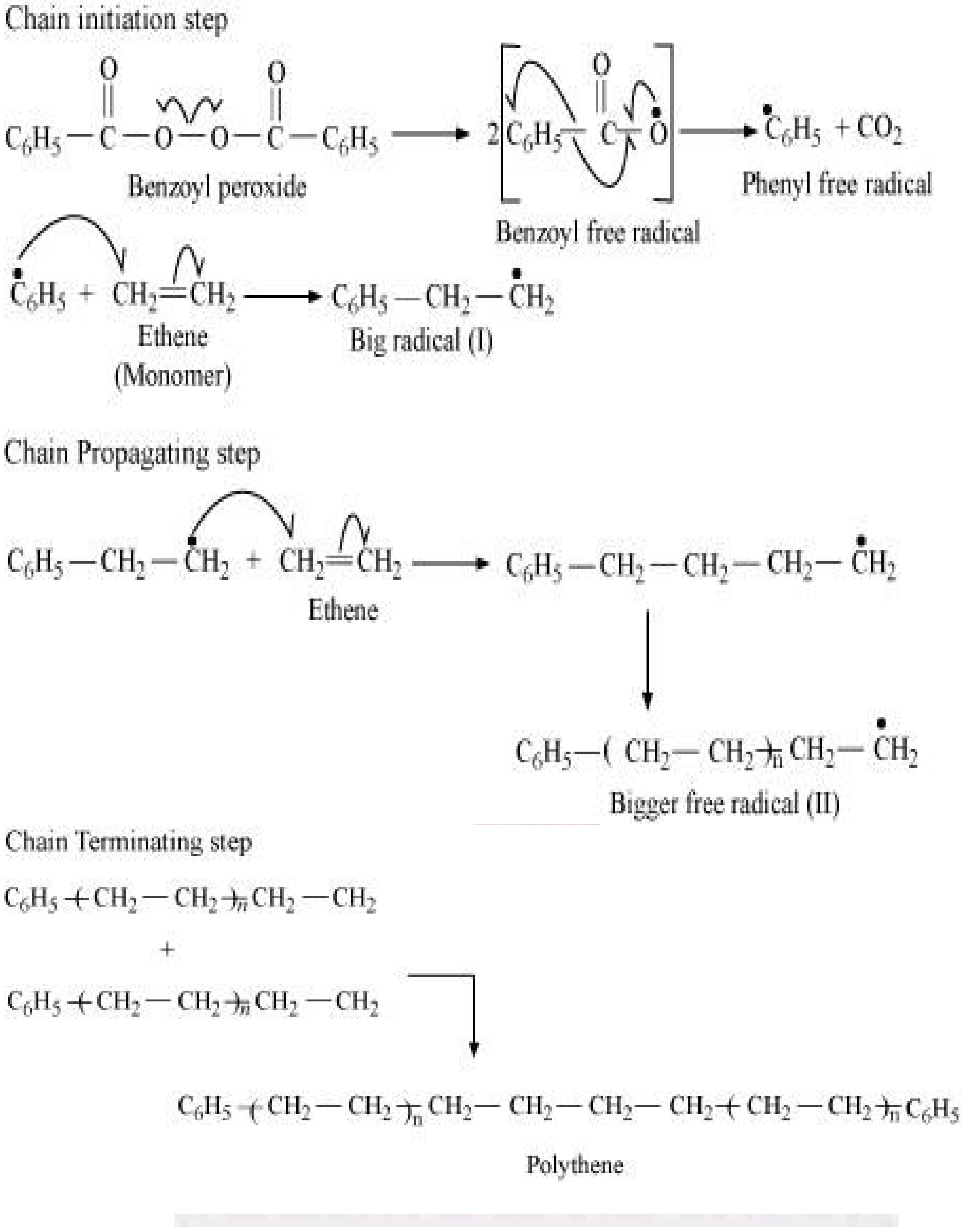
Types of polymerisation:

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

Free Radical Polymerisation: Free radical polymerisation takes in the presence of catalysts such as benzoyl peroxide.

For example polymerisation of ethene is carried out at high temperatures and pressure in the presence of benzoyl peroxide.

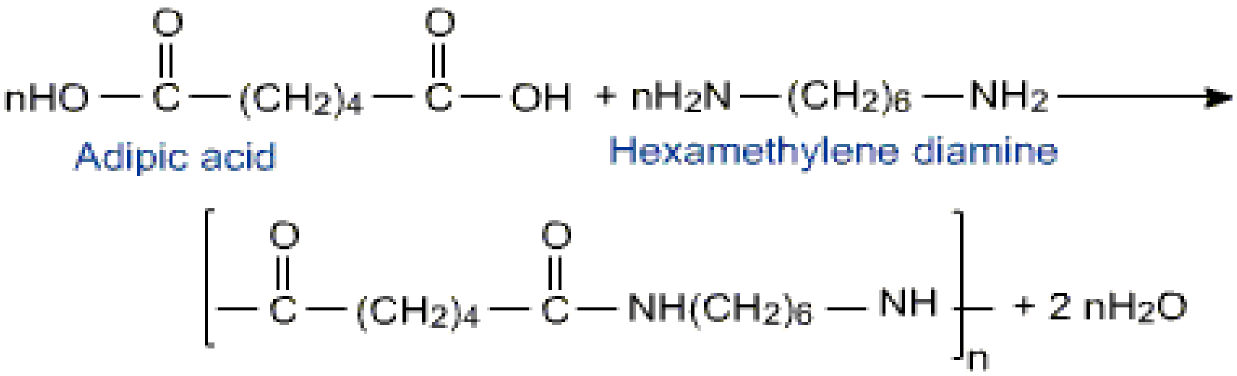
Mechanism : Free radical mechanism involves three steps.



Condensation polymerisation: A polymer formed by reaction occurring between monomers which contain polar functional groups with the elimination of small molecules like water, HCl, NH3, etc. called condensation polymerisation.
Examples: Nylon 6:6, terylene, etc.

Nylon 6:6:

Preparation: Nylon 6: 6 formed by adipic acid & hexamethylenediamine.



$$nHO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + nH_2N-(CH_2)_6-NH_2 \longrightarrow \left[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH(CH_2)_6-NH\right]_n + 2\,nH_2O$$

Properties:

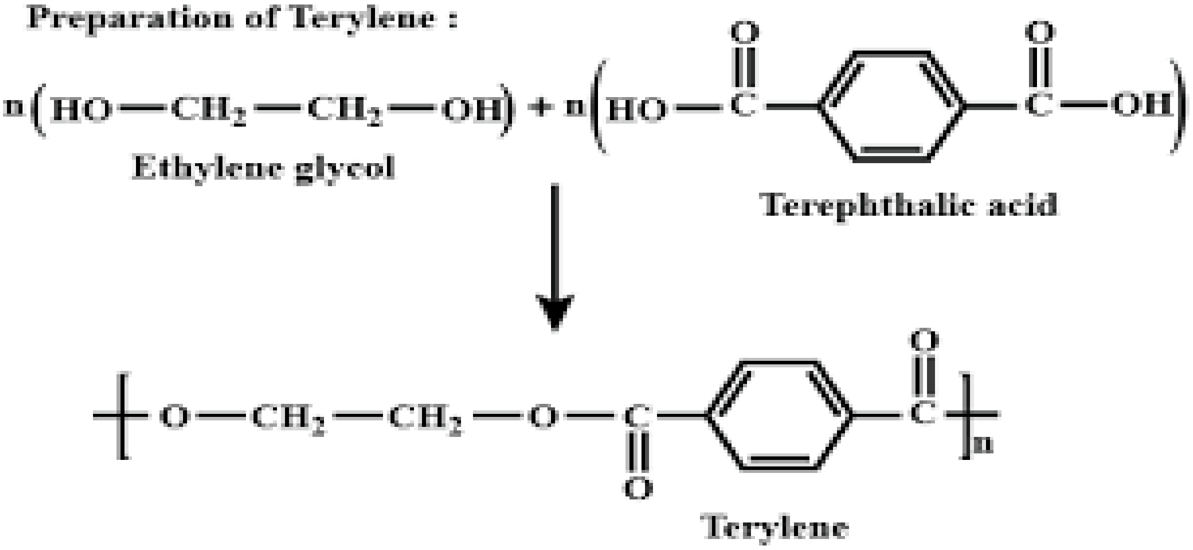
- They are translucent, whitish, horn
- High temperature stability
- Good abrasion resistance
- Insoluble in solvents
- High tensile strength

Applications:

- Making socks, ladies hoses, dresses, carpets etc.
- Making threads, ropes, filaments.
- Making strings for musical instruments, surgical sutures.
- Toothbrush bristles.

Terylene:

Preparation: Terylene is formed by ethylene glycol and terephthalic acid



Properties:

- High stretch resistance
- High wrinkle resistance
- Highly resistant to mineral acids and organic acids

Applications:

- For manufacturing clothing
- For blending with wool to provide crease and wrinkle resistance.
- For blending with cotton
- As glass reinforcing material in safety helmets.

Difference between thermoplastic and thermosetting polymer

Thermoplastic plastics	Thermosetting plastics
1) Such polymers or plastics are usually formed by addition polymerisation.	1) These plastics are usually formed by condensation polymerisation.
2) They are linear or slightly branched long chain polymers.	2) They are cross linked or heavily branched.
3) They can be easily soften on heating and hardened on cooling.	3) They cannot be softened on heating On prolonged heating they burn.
4) They are held together by Van der Waal forces of attraction.	4) They are held together by strong hydrogen bonds.
5) By nature they are soft, weak and less brittle.	5) They are strong, hard and more brittle in nature.
6) They can be reshaped and reused.	6) They cannot be reshaped and reused.
7) Their molecular weight is low.	7) Their molecular weight is large.
8) They are quite soluble in organic solvents.	8) They are insoluble in organic solvents.
9) They can be remoulded into desired shapes.	9) They cannot be remoulded.
10) Examples: polythene, polystyrene, polyvinyls, etc.	10) Examples: bakelite, urea-formaldehyde resins, etc.

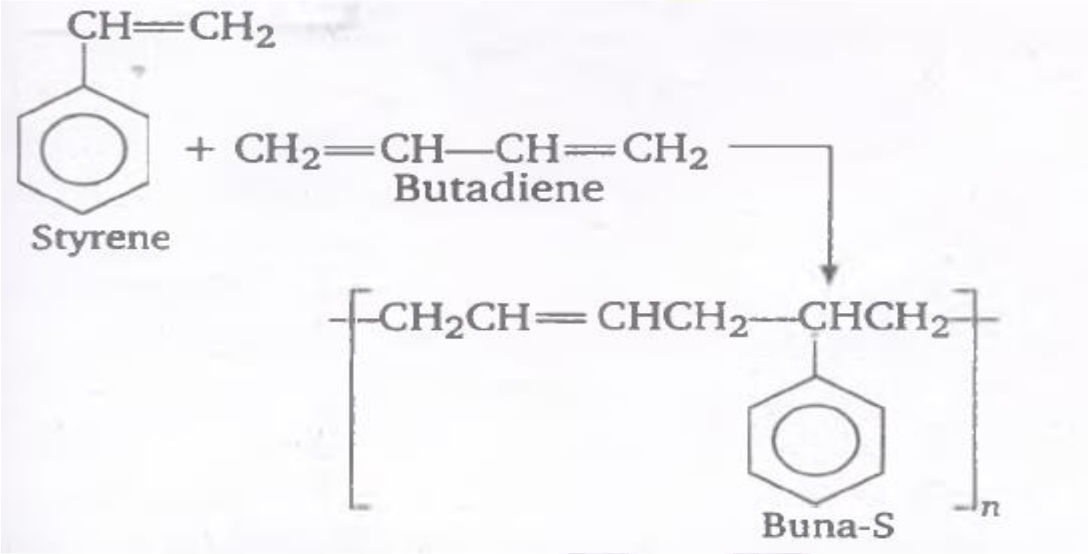
Elastomers:

- 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.

BUNA-S:

Preparation: Buna-S is produced by copolymerisation of butadiene and styrene.

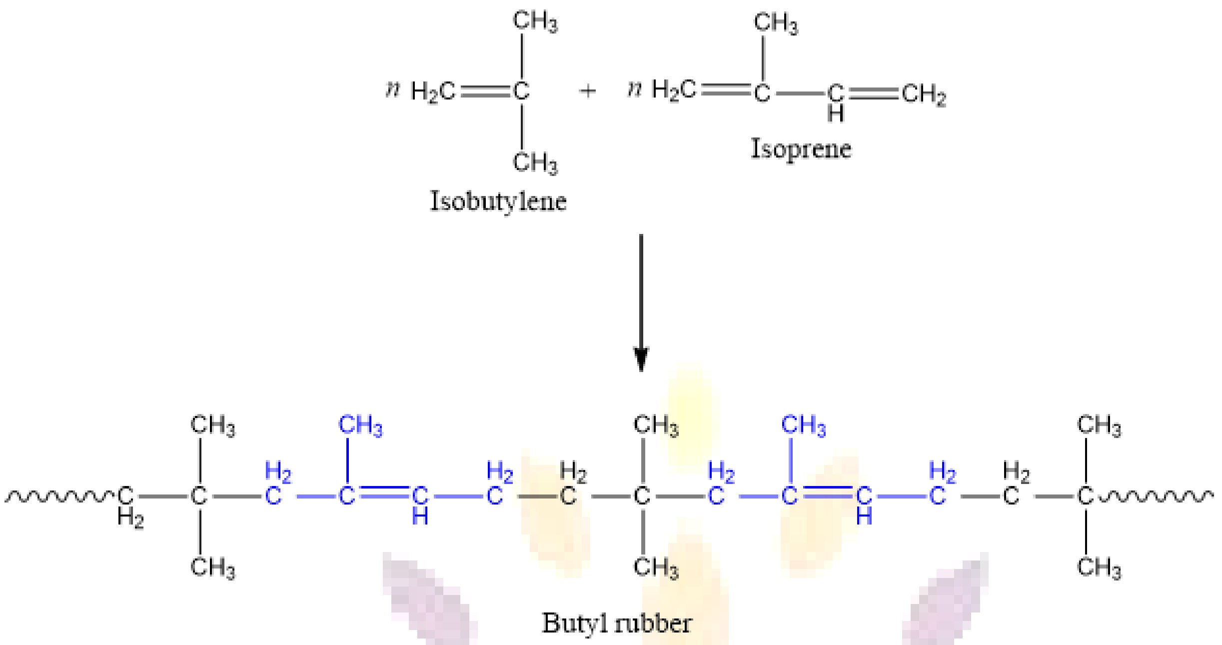


Properties:
- High abrasion resistance
- High load bearing capacity
- High resilience
- Readily oxidised in the presence of ozone
- Swells in oils and solvents
- Can be vulcanised

Applications:
- Manufacturing motor tyres
- Floor tiles
- Shoe soles
- Gaskets
- Foot wear
- Wire and cable insulation
- Adhesives
- Tank linings

Butyl rubber:

Preparation: Butyl rubber is made by copolymerisation of isobutene and isoprene



Properties:

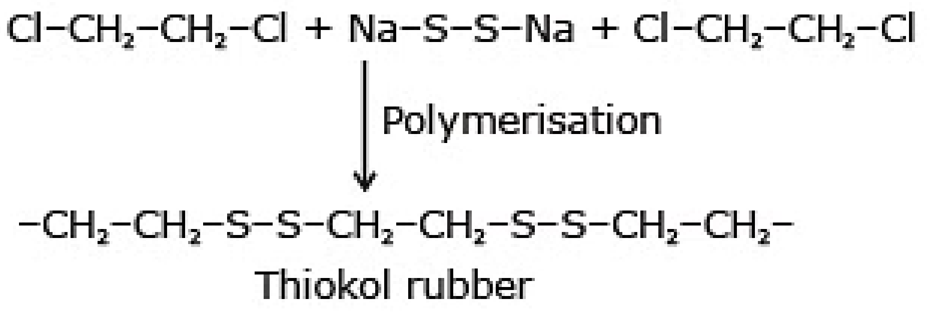
- Excellent resistant to heat
- Resistant to abrasion
- Resistant to chemicals
- Resistant to polar solvents
- Resistance to ozone
- Good electrical insulator
- Can be vulcanised
- Low permeability to air and gases.

Applications: For making

- cycle and automobile tubes
- Automobile parts
- Hoses
- Conveyor belts
- Tank linings
- Insulation for high voltage wires and cables

Thiokol rubber:

Preparation: It is made by sodium poly sulphide and ethylene dichloride



Properties:

- Good resistance to mineral oils
- Resistant to fuels
- Resistant to solvents
- Resistance to oxygen, ozone, sunlight
- Impermeable to gases
- Cannot be vulcanised
- Poor abrasion resistance
- Poor strength

Applications:

- Used as a solid fuel in rocket engines
- Engine gaskets
- For making hoses
- Tank lining
- Used as a sealant

Bakelite:

Preparation :

- It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst.
- The initial reaction results in the formation of O- and P- hydroxyl methyl/phenol which reacts to form linear polymer.
- During modeling hexamethylene tetramine is added, which converts to insoluble solid of cross-linked structure Bakalite.
- Commercially these are available into two forms nova lacks & resols.

Properties.

- Phenolic resins are hard, rigid and strong materials They have excellent heat and moisture resistance.
- They have good chemical resitance.
- They have good abrasion resistance.
- They have electrical insulation characteristics
- They are usually dark coloured.
- Lower molecular weight grades have excellent bonding strength and adhesive properties.

Uses:

- Phenol formaldehyde resins are used for
- Domestic plugs and switches
- Handles for cooker and saucepans.
- Distributor heads for cars
- Adhesives for grinding wheels and brake linings.Varnishes, electrical insulation and protective coatings.
- The production of ion exchange resins.

PVC :

- Poly Vinyl Chloride is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide in an auto clave under pressure. Vinyl chloride, so needed is generally prepared by treating acetylene at 1 to 1.5 atmospheres with hydrogen chloride at 600C to 800C in the presence of metal chloride as catalyst

Properties:

- It occurs as a colourless rigid mater
- It is having high density and low softening point.
- It is resistant to light, atmospheric oxygen, inorganic acids and alkalis.
- It is most widely used synthetic plastic

Uses:

- It is mainly used as cable insulation, leather cloth, packing and toy
- It is used for manufacturing of film, sheet and floor covering.
- PVC pipes are used for carrying corrosive chemicals in petrochemical factories.

TEFLON OR Poly tetra fluoro ethylene:

Teflon is obtained by polymerization of water-emulsion tetrafluoroethylene, under pressure in presence of benzoyl peroxide as catalyst.

Properties:

- Due to the presence of highly electronegative fluorine atoms and the reqular configuration of the polytetrafluoro ethylene molecule results in very strong attractive forces between the different chains.
- These strong attractive forces give the material extreme toughness, high softening point
- exceptionally high chemical-resistance towards all chemicals, high density, waxy touch, and very low coefficient of friction,
- extremely good electrical and mechanical properties: It can be machined, punched and drilled.
- The material, however, has the disadvantage that it cannot be dissolved and cannot exist in a true Molten state.
- Around 3500 c, it sinters to form very viscous, opaque mass, which can be moulded into certain forms by applying high pressures.

Uses:

- as insulating material for motors, transformers, cables, wires, fittings, etc,
- making gaskets, packing, pump parts, tank linings, chemical-carrying pipes, tubing's and tanks, etc,; for coating and impregnating glass fibres, asbestos fibres and cloths; in non-lubricating bearings and non-sticking stop-cocks etc.

Natural Rubber:

Rubbers also known as Elastomers, they are high polymers, which have elastic properties in excess of 300%.Natural rubbers consist of basic material latex, which is a dispersion of isoprene. During the treatment, these isoprene molecules polymerize to form, long-coiled chains of cis-polyisoprene. Natural rubber is made from the saps of a wide range of plants like Hevea brasillians and guayule.

Latex: is a milky white fluid that oozes out from the plant Hevea brasillians when a cut is made on the steam of the plant.The latex is diluted with water. Then acetic or formic acid is added [1kg of acid per 200kgs of latex] to prepare coagulum. This is processed to give wither crepe rubber or smoked rubber.

Natural rubber: Natural rubber is found in several species of rubber trees grown in tropical countries of these Hevea brasiliensis is the most important source of natural rubber and the rubber obtained from this is known as "Hevea" rubber. Rubber is stored in the form of white fluid called 'latex' behind the bark of the rubber tree. Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene). It is a hydrocarbon polymer having molecular formula (C_5H_8)n. Polyisopren eexists in two geometric isomers cis and transforms. Natural rubber is soft and has cis-configuration while 'Guttapercha' or, 'Ballata' has trans configuration.

Properties:

- It is hard and brittle at low temperature and soft and sticky at high temperature. It is soft and soluble in many hydrocarbon solvents and carbon disulphide (CS_2)It has high water absorption power.

- It is a sticky substance, rather difficult to handle It is readily attacked by acids and alkalies.
- It has low tensile strength.
- It has poor abrasion resistance.
- It is sensitive to oxidative degradation

Vulcanization:

Vulcanization is a process of heating the raw rubber at 100 – 140oC with sulfur for 1 – 4 hours. The sulfur combines chemically at the double bonds of different rubber molecules and provides cross-linking between the chains. The degree of vulcanization depends on the amount of sulfur used. Tyre industry uses 3 – 5% sulfur.
If the amount of sulfur is increased to 30%, a hard and rigid rubber called "ebonite" is produced.

Advantages of vulcanization:

- The tensile strength of vulcanized rubber is very good. It is 10 times the tensile strength of raw rubber.
- It has excellent resilience i.e., articles made from it returns to the original shape when the deforming load is removed.
- It has better resistance to moisture, oxidation, abrasion.
- It has much higher resistance to wear and tear compared to raw rubber.
- It has broader useful temperature range (-40 to 100oC) compared to raw rubber's useful temperature range (10 – 60oC).
- It is a better electrical insulator Ex: Ebonite It is resistant to i) Organic solvents like petrol, benzene, CCl4, ii) Fats and oils, but it swells in them.
- It has only slight tackiness.
- It has low elasticity. They property depends on the extent of vulcanization. Ebonite has practically no elasticity.
- It is very easy to manipulate the vulcanized rubber to produce the desired shapes.

Conducting polymers:

Definition: A polymer that can conduct electricity is known as conducting polymer.
Classification:
Conducting polymers can be classified as follows.

Intrinsically conducting polymers: The polymers have extensive conjugation in the backbone which is responsible for conductance. These are of two type Conducting polymers having conjugated - electrons in the backbone: Such polymers contain conjugated – electrons in the back bone which increases their conductivity to a large extent Explanation: Overlapping of conjugated -electrons over the entire backbone results in the formation of valence bandswell as conduction bands that extends over the entire polymer molecule.
The valence band and the conduction bands aseparated by a significant band gap. Thus, electrical conduction occur only after thermal or photolytic activation electrons to give

them sufficient energy to jump the gap and reach into the lower levels of the conduction band. All the three forms of polyanilines have conductivities of the order of 10 -10 Scm-1. conductivity of these polymerhaving conjugated -electrons in the backbone is not sufficient for their use in different applications.

Applications of Conducting Polymers:-

- In rechargeable Light weight batteries based on perchlorate doped Polyacetylene-lithium Systems: These are about 10 times lighter than convensional lead storage batteries.
- These can produce current density up to 50mA/cm2.
- In electrochromic displays and optical filters: ICP’s can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters.
- Thus the conducting polymers can be used as electro chromic materials i.e., the materials that change colour reversibility during the electrochemical processes of charge and discharge.
- In wiring in aircrafts and aerospace components.
- In telecommunication systems.
- In electromagnetic screening materials.
- In electronic devices such as transistors and diodes.
- IN solar cells, drug delivery system for human body etc., In photovoltaic devices.

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 C_nH_m. Hydrocarbon fuels exist in all phases, some examples being coal, gasoline (usually treated as octane C_8H_{18}), 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

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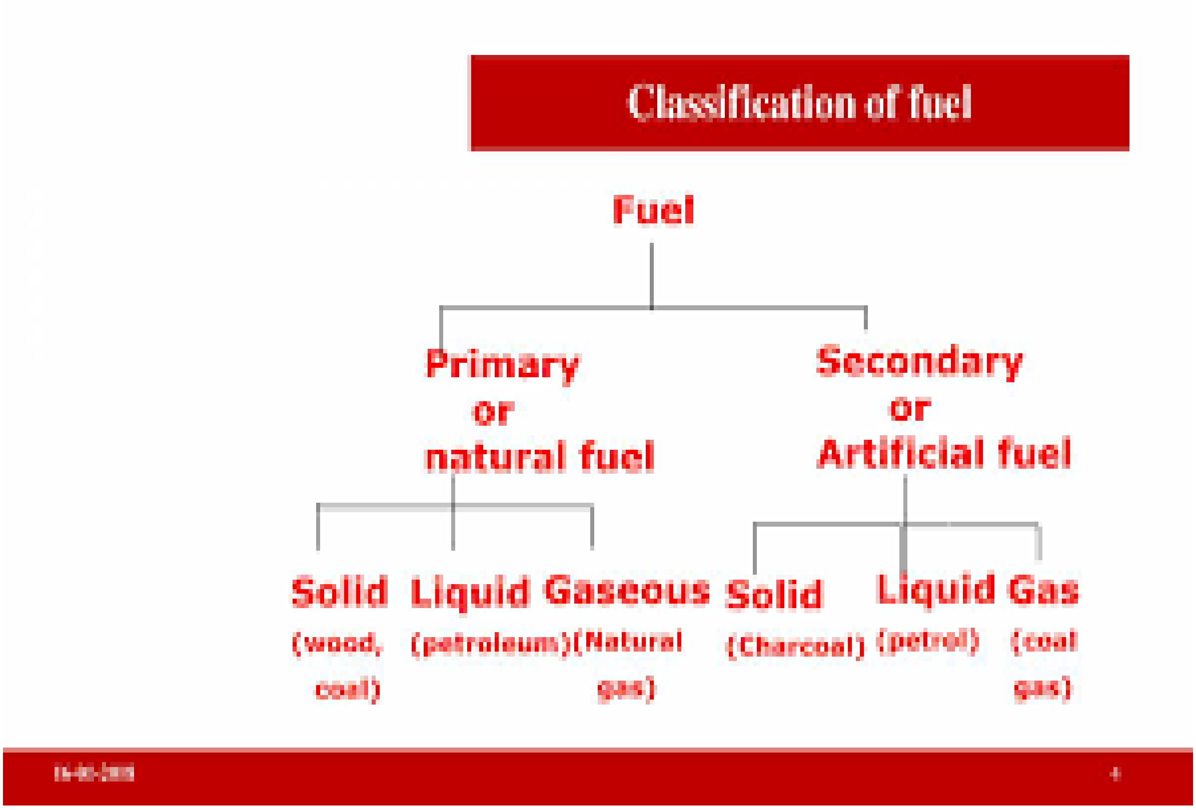


Classification of fuel

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.

$N.C.V = G.C.V - 9\times(H/100)\times587$ Where H= % of Hydrogen in the fuel)

(Or)

$N.C.V = G.C.V - 0.09\times H\times587$

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.

<u>Moisture</u> :-Step-1 1 gm of air dried coal powder taken into crucible which is heated on electrical oven at 105 ^{o}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

<u>Volatile matter</u>:

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)

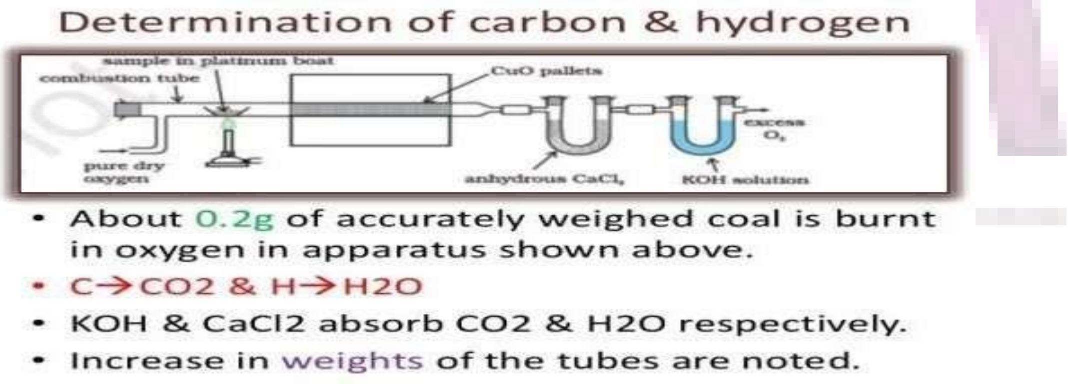
Good quality of coal has more fixed carbon

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 hydrogen



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× 12/44

%hydrogen = increased weight of $CaCl_2$ bulb/weight of coal taken$\times 2/18$

<u>Nitrogen:</u> % 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$\times 14 \times 100$ / weight of coal taken $\times 1000$

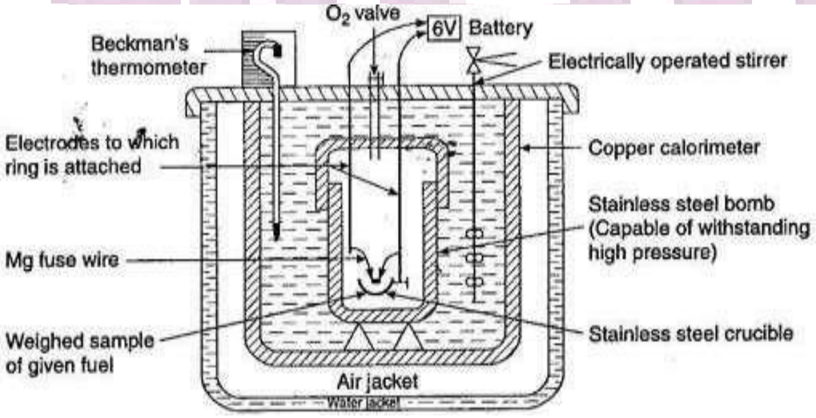
<u>Sulphur</u>: sulphur is present on coal is estimated by gravimetrically
A known coal sample burnt in bomb calorimeter, if sulphur is present to give sulphates, sulphides etc, which are followed the treatment with $Bacl_2$ to give the barium sulphate precipitation, and it is dried out and weighed out

% of the sulphur=weight of $Baso_4$$\times 32 \times 100$/weight of coal taken $\times 233$

<u>Ash</u>:% of ash=weight of ash residue /weight of coal taken$\times 100$
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)

<u>Determination of solid or non volatile liquid fuel calorific value by bomb calorimeter</u>



- 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:

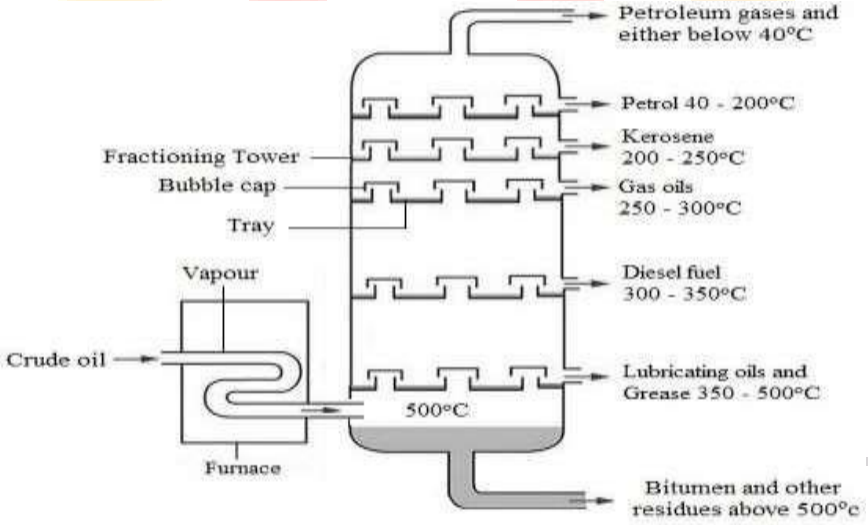
separation of water by coteril's method:

- 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°c 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**

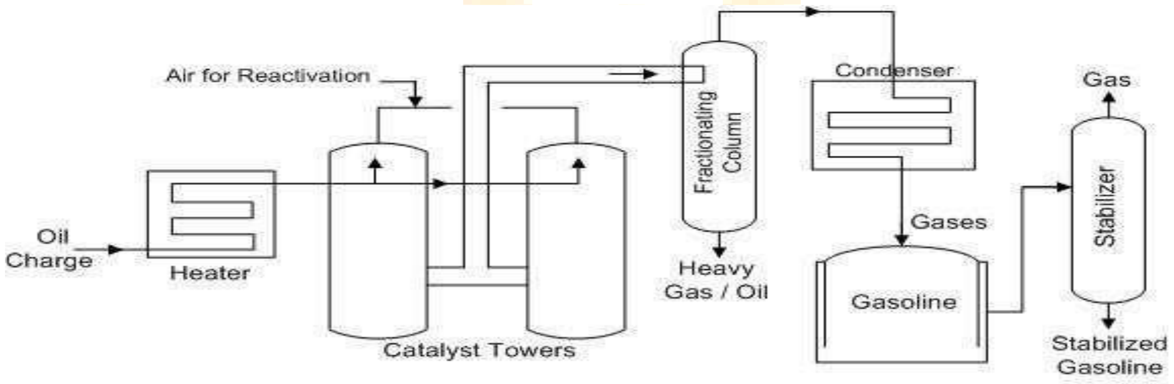
Catalytic cracking: in this type cracking catalysts are used:

- 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:

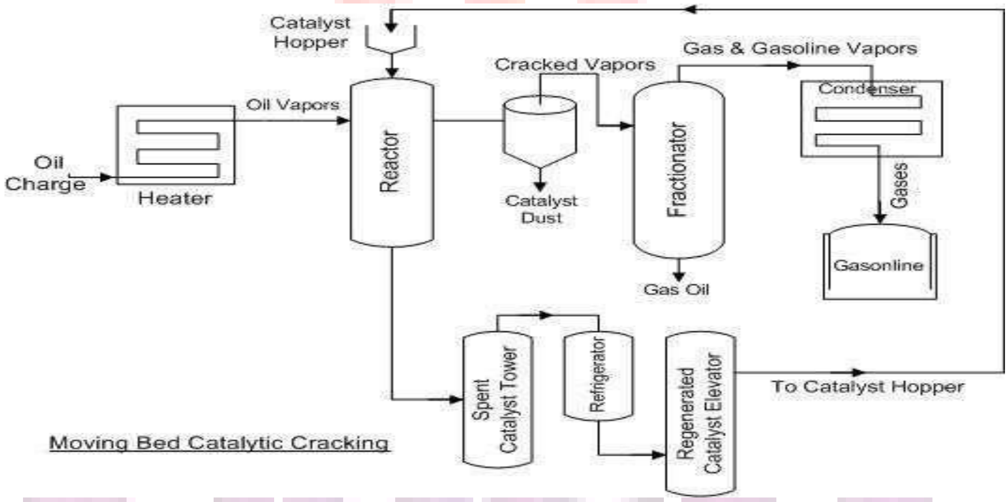


Fixed Bed Catalytic Cracking

- The oil vapour are heated in pre heater about 425-450°*c*
- The hot vapours are forced to catalyst chamber (containing artificial clay+zro_2) maintained at 425-450°*c* 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 $500°c$ 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 $600°c$ 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:

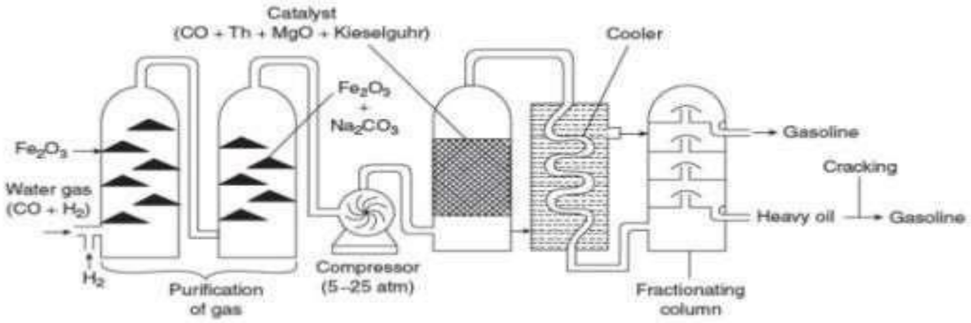
1. Fisher tropsch method 2. **Bergius process**

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°*c*
- 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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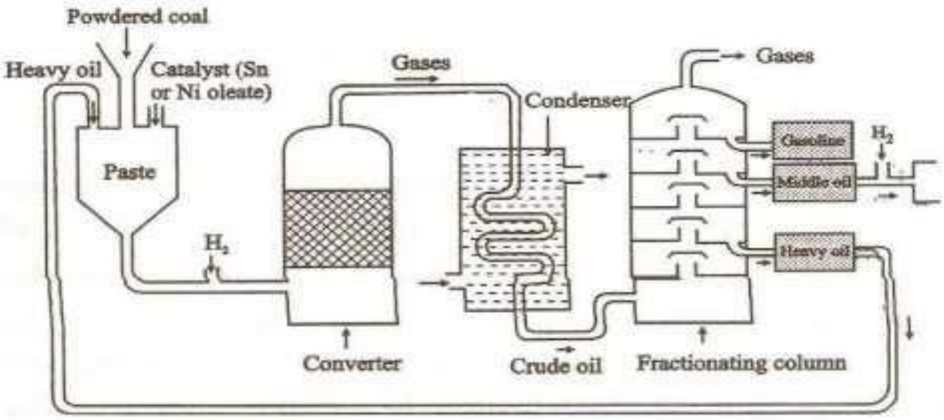
2. Bergius process for Synthetic Petrol



- 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°*c* and 200-250°*c*
- 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:

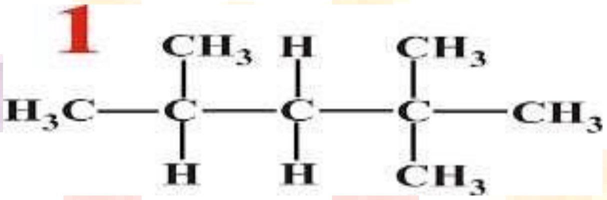
1. Good quality of fuel with higher octane number 2.by adding anti knocking reagents

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→** *iso Octene*



(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:

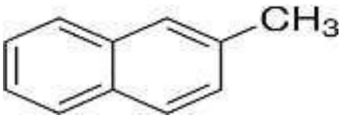
It is to be decided that the quality of diesel when diesel oil contain the branched chain hydro carbon shows knocking

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---
2. Wet or reign gas: natural gas contain CH_4 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

1. LPG is used as domestic fuel and as fuel for internal combustion engine
2. it is used in hydrolysis process
3. LPG is used in industries as welding annealing ,cutting cl^-

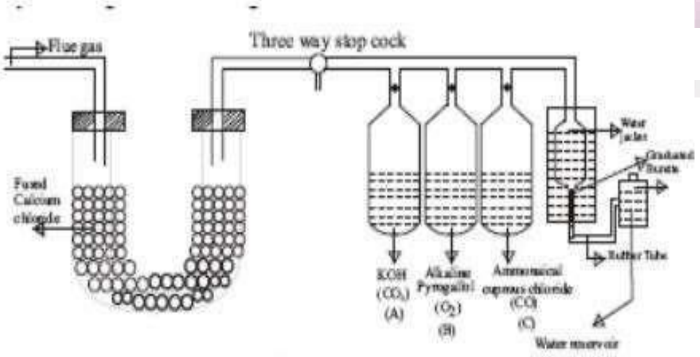
C.N.G (compressed natural gas):

1. When natural gas (CH_4) is compressed at high pressure (1000 atm) or cooled to -160°c it is converted in CNG
2. it is stored in cylinder made of steel
3. it is now replacing gasoline (petrol) as it releases less pollutants during combustion c.n.g vehicles are used to reduce the pollution

<u>Advantages:</u>

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 => $g = a / mv \times 100$.

a. Where a=amount of the gas in the bulb. m=mass of the gas in the bulb.
b. 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 ($SiO2$) : 20-24%
iii) Alumina ($Al2O3$) : 5-7.5%
iv) Magnesia (MgO) : 2-3%
v) Ferric Oxide ($Fe2O3$) : 1-2.5%
vi) Sulphur trioxide ($SO3$) : 1-1.5%
vii) Sulphur Oxide ($Na2O$) : 1%
viii) Potassium Oxide ($K2O$) : 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.

$3CaO.Al2O3 + 6H2O \rightarrow 3CaO.Al2O3.6H2O + Heat$

$2(2CaO.SiO2) + 4H2O \rightarrow 3CaO.2SiO2.6H2O + Ca(OH)2 + Heat$

$4CaO.Al2O3.Fe2O3+7H2O \rightarrow Ca3Al2O6.6H2O + CaO.Fe2O3.H2O + Heat$

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

$2(2\ CaO.SiO2) + 6H2O\ 3CaO.2SiO2.3H2O + 3Ca(OH)2 + Heat$

$3CaO.Al2O3 + 6H2O \rightarrow 3CaO.Al2O3.6H2O + Heat$

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

$3CaO.Al2O3 + xCaSO4.2H2O\ 3CaO.Al2O3.\ xCaSO4.2H2O$

Lubricants

A lubricant may thus be defined as a substance which reduces the friction when introduced between two surfaces.

Functions of lubricants:

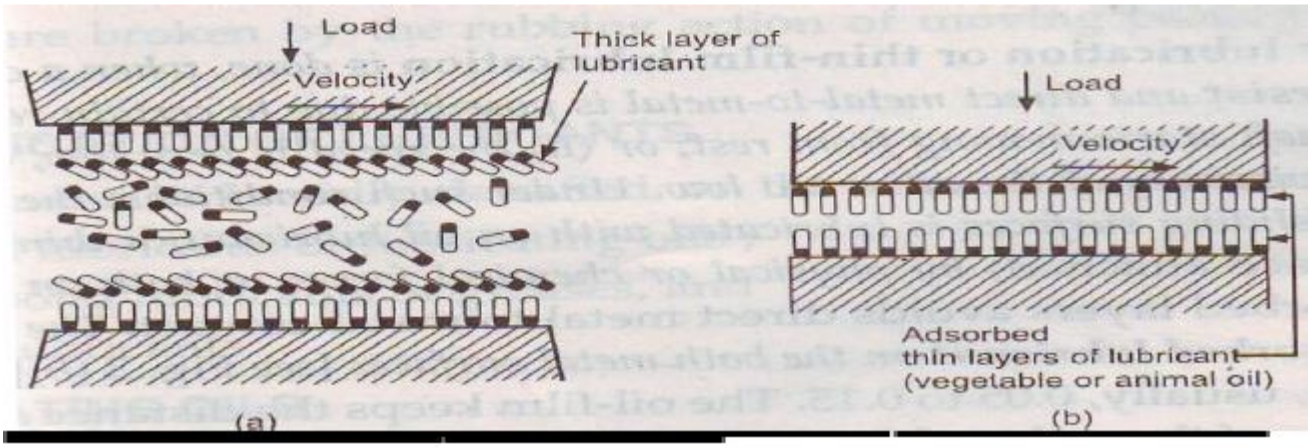
- It reduces the maintenance and running cost of the machine.
- It reduces unsmooth relative motion of the moving surfaces.
- It reduces the loss of energy in the form of heat that is it acts as a coolant.
- It reduces waste of energy, so that efficiency of the machine is increased.
- It reduces surface deformation, because the direct contact between the moving surfaces is avoided.
- It reduces the expansion of metals by local frictional heat.
- In some times, it acts as a seal, preventing the entry of dust and moisture between the moving surfaces.
- It minimizes corrosion.

Types of Lubrication

a. Hydrodynamic or fluid film or Thick-Film lubrication b. Boundary or Thin-Film lubrication. Extreme pressure lubrication:

A. Hydrodynamic or fluid film or Thick-film lubrication

In this, the moving/sliding surfaces are separated from each other by a bulk lubricant film (at least 1000oA thick).This bulk lubricant film prevents direct surface to surface contact so that the small peaks and valleys do not interlock. This consequently reduces friction and prevents wear. Fluid film lubrication is shown in figure. The small friction is only due to the internal resistance between the particles of the lubricant moving over each other. In such a system, friction depends on the thickness and viscosity of the lubricant and the relative velocity and area of the moving/sliding surfaces the co-efficient of friction is as low as 0.002 to 0.03 for fluid film lubricated system.Ex: how fluid film is actually generated between a bearing and a rotating journal.Shows a journal resting on the bottom of the bearing before motion. The oil film which separates the surfaces when the journal rotates. Simplified drawing of this process that shows how, after start up, the journal begins to climb up one side of the bearing; as its pumping action draws oil under it, the journal is forced to the other side by the “oil wedge”.At start up the coefficient of friction is high in the presence of boundary lubrication. After start up however the coefficient falls rapidly. This is due to the fact that metal surfaces do not come into direct contact with each other. The resistance to movement is only due to the internal resistance.



B. Boundary or Thin-Film lubrication:

When the lubricant is not viscous enough to generate a film of sufficient thickness to separate the surfaces under heavy loads, friction may yet be reduced with the proper lubricant. Such an application is known as boundary lubrication.A thin later of lubricant is adsorbed on the metallic surfaces which avoids direct metal to metal contact. The load is carried by the later of the adsorbed lubricant on both the metal surfaces. In boundary lubrication, the distance between moving/ sliding surface is very small of the order of the height of the space asperities. The contact between the metal surfaces is possible by the squeezing out of lubricating oil film. When this occurs the load would be taken on the high spots of the journal and the bearing, and the two surfaces tend to because welded together by appreciable heat generated. This prevents motion as the two surfaces adhere together.For boundary lubrication the lubricant molecules should have ling hydrocarbon chains,high viscosity
index, resistance to heat and oxidation, good oiliness, low pour and oxidation.Graphite and MoS_2, Vegetable and animal oils and their soaps are used for boundary lubrication.

C. Extreme pressure lubrication:

Is done by incorporating extreme pressure additives in mineral oils for applications in which high temperature is generated due to high speed of moving/sliding surfaces under high pressure.Chlorinated esters, sulphurised oils and tricresyl phosphate are examples of such additives.These additives react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulfides or phosphates in the form of durable film. These films can withstand very high loads and high temperatures.Applications: wire drawing of titanium, in cutting fluids in machining of tough metals, for hypoid gears used in rear axle drive of cars.

Classification of Lubricants:

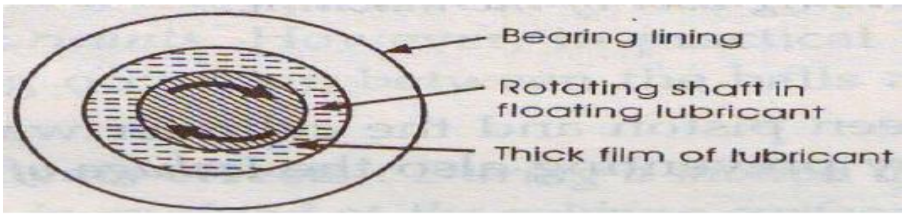
Lubricants are classified on the basis of their physical state as follows

- Liquid Lubricants or Lubricating Oils
- Semi-Solid Lubricants or greases
- Solid Lubricants.

1. Liquid Lubricants or Lubricating Oils:

Lubricating oils reduce friction and wear between two moving metallic surfaces by providing a continuous fluid film in between the surfaces. A good lubricant must have the following characteristics.

- **a.**It must have high boiling point or low vapour pressure.
- **b.**Thermal stability and oxidation resistance must be high.**c.**It must also have adequate viscosity for particular operating condition
- **d.**The freezing point must be low.
- **e.**It must also have non-corrosive property lubricating oils are further sub-classified as



A. **Animal and Vegetable oils:**

Animal and vegetable oils are triglycerides of higher fatty acids.They have very good oiliness. However, they are costly, undergo oxidation very easily, and have a tendency to hydrolyze when it contact with moist air or water.These oils undergo decomposition on heating without distilling, and hence they are“fixed oils”. They are used as additives to improve the oiliness of petroleum oils.

B.Petroleum oils or Mineral oils: They are obtained by fractional distillation of crude petroleum oils. The length of the hydrocarbon chain varies between C12to C50

They are cheap and quite stable under operating conditions. They possess poor oiliness, the oiliness of which can be improved by the addition of higher molecular weight vegetable or animal oils. Crude liquid petroleum oil cannot be used as such, because they contain lot of impurities like wax. Asphalt, colored substances and other oxidisable impurities.

C.Blended oils or Additives for lubricating oils:

No single oil serves as the most suitable lubricant for many of the modern machinery. Specific additives are incorporated into petroleum oils to improve their characteristics. These oils ar e to improve their characteristics. These oils are called “blended oils” and give desired lubricating properties,required for particular machinery.

Synthetic lubricants:

Mineral oils cannot be used effectively as they tend to get oxidized at very higher temperatures while wax separation will occur at very low temperatures. so,synthetic lubricants have been developed, which can meet the severe operating conditions such as in aircraft engines. The same lubricants may have to be in the temperature range of -500C to 2500

Poly glycol ether, fluoro and chloro hydrocarbons, organophosphate silicone are currently used as synthetic lubricants.

2. Semi-Solid Lubricants or greases:

Grease is a semi solid lubricant obtained by thickening liquid lubricating oil through the addition of a metallic soap. The thickness is usually sodium or calcium or lithium soap.

Types of grease:

a. Soda-base grease
b. Lime-base greasec. Lithium-soap greased.
c. Barium-soap greasee. Axle (Resin) grease

3. **Solid Lubricants:**. Solid lubricants are used where

- The operating temperature and load is too high.
- Contamination of lubricating oils or greases by the entry of dust or grit particles are avoided.
- Combustible lubricants must be avoided.Graphite and Molybdenum disulphide are the widely used solid lubricants.

Graphite: It consists of a multitude of flat plates, which are held together by weak Vader Walls forces, so the force to shear the crystals parallel to the layers is low. it is used either in powder form or as suspension. When graphite is dispersed in oil, it is called ‘oil dag’

when graphite is dispersed in water is called ‘aquadag’. it is ineffective at above 3700C. It is used for lubricating internal combustion engines.

Molybdenum disulphide: It has a sandwich like structure in which a layer of molybdenum atoms. Lies between two layers of sulphur atoms. The weak Vader Waals forces, acting in between the layers, can be destroyed easily.

Properties of lubricants

1. Viscosity:

Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of a lubricating oil, the lower the viscosity, greater the flow ability. If temperature increases viscosity of the lubricating oil decreases. And pressure increases, viscosity of the lubricating oil increases.

2. Viscosity index:

The rate at which the viscosity of oil changes with temperature is measured by an empirical number, known as the viscosity-index. A relatively small change in viscosity with temperature is indicated by high viscosity index. Whereas a low viscosity index shows a relatively large change in viscosity with temperature.

3. Flash and fire point:

The flash point of oil is the lowest temperature at which it gives off vapors that will ignite for a moment when a small flame is brought near it.The fire point of an oil is the lowest temperature at which the vapors of the oil burn continuously for at least 5 seconds when a small flame is brought near it.The flash and fire points are used to indicate the fire hazards of petroleum product and evaporation losses under high temperature operations. Knowledge of flash and fire points in lubricating oil helps to take preventive measures against fire hazards.

4. Cloud and pour point:

The cloud point of petroleum oil is the temperature at which solidifiable compounds, like paraffin wax, present in the oil begin to crystallize or separate from solution.The pour point of petroleum oil is the temperature at which the oil ceases to flow or pour.Cloud and pour points indicate the suitability of lubricants in cold conditions.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