# UNIT - II

# ENGINEERING MATERIALS

# POLYMERS

## Introduction

The term ‘polymer’ derived from the Greek words

Poly → many

mer → Repeating unit

# POLYMERS

**Polymer – Definition:**

Polymers are the substances consisting of giant or macromolecules made by linking a large number of smaller molecules (monomers)

Monomer: monomer is a single unit of polymer which is repeated in the polymer & which makes up the polymer

Polymerisation:

Polymer is molecule formed by joining of thousands of smaller molecular units together by chemical bonds.

A chemical process that leads to the formation of polymer is known as polymerizatin.

**Degree of polymerization:** The number of repeating units (or) monomeric units available in the polymer is known as degree of polymerization

# Functionality

The number of bonding sites

or

The number of reactive sites

or

The number of functional groups in a monomer is known as functionality

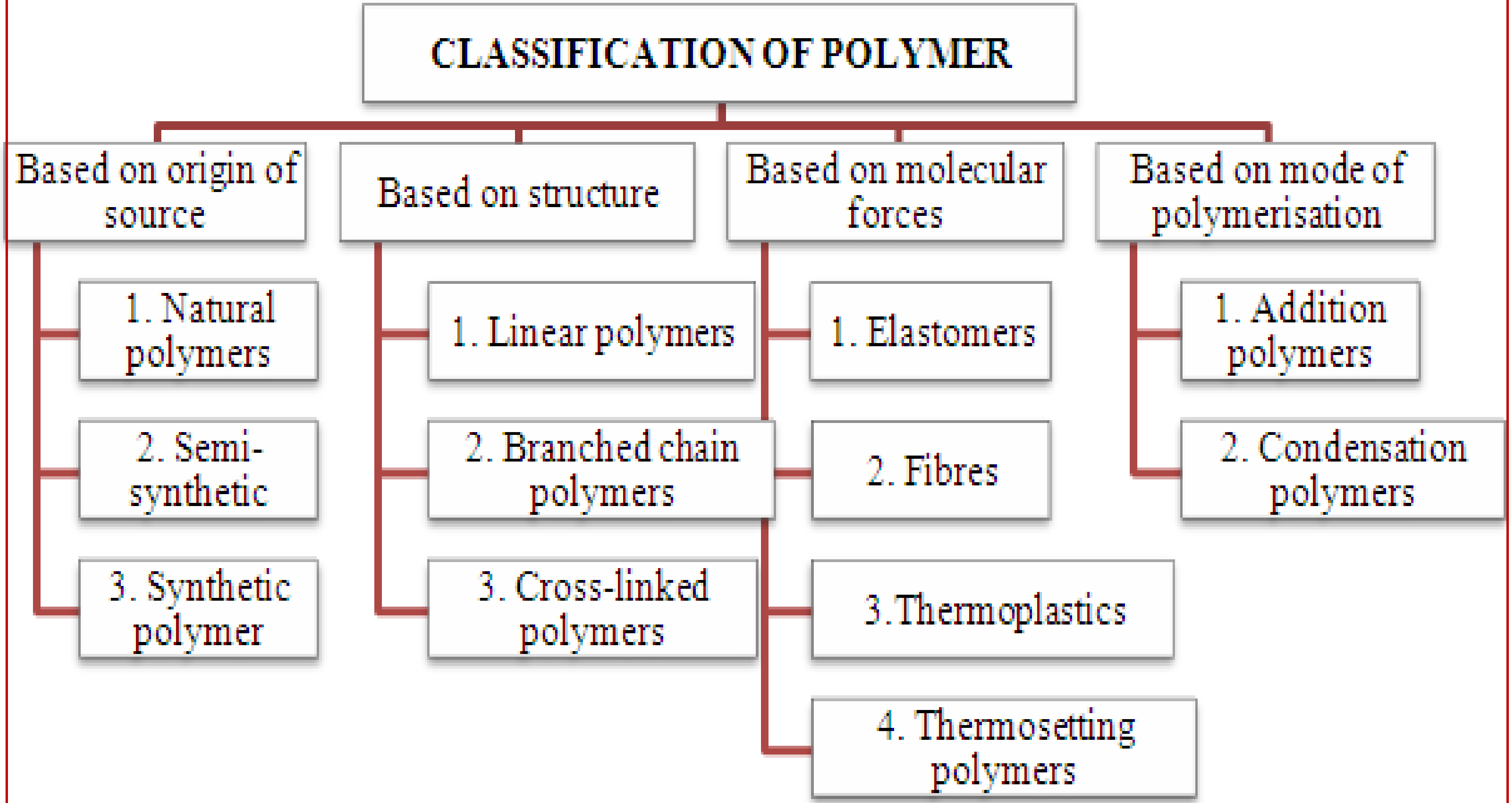
Ex:

$CH_2 = CH_2$ (ethylene) – Functionality is 2 (Two bonding sites are due to the presence of one double bond in the monomer. Therefore ethylene is a bifunctional monomer)

If the functionality of monomer is two linear polymer is formed

If the functionality of monomer is three cross linked polymer is formed

- ✓ Polymers with a high degree of polymerization are called **‘high polymers’**
- ✓ and those with low degree of polymerization are called ‘**oligomers**’**.**
- ✓ **High polymers have** very high molecular weights ($10^4$ to $10^6$) and hence are called as **‘macromolecules**’**.**



# CLASSIFICATION OF POLYMER

- Based on origin of source
  - 1. Natural polymers
  - 2. Semi-synthetic
  - 3. Synthetic polymer
- Based on structure
  - 1. Linear polymers
  - 2. Branched chain polymers
  - 3. Cross-linked polymers
- Based on molecular forces
  - 1. Elastomers
  - 2. Fibres
  - 3. Thermoplastics
  - 4. Thermosetting polymers
- Based on mode of polymerisation
  - 1. Addition polymers
  - 2. Condensation polymers

Depending upon the intermolecular forces, the polymers have been classified into 3 types.

1. Elastomers
2. Fibers
3. plastics (Thermoplastic & Thermo setting)

1. **Elastomers :** The polymers that have elastic character like rubber (a material that can return to its original shape after stretching is said to be elastic) are called elastomers. In elastomers the polymers chains are held together by weak intermolecular forces. Because of the presence of weak forces.

Example: natural rubber.

**2.Fibers :** These are the polymers which have strong intermolecular forces between the chain. These forces are either hydrogen bonds or dipole-dipole interaction. Because of strong forces, the chains are closely packed giving them high tensil strength and less elasticity.

-

- Example: Nylon 66, dacron, silk etc.

## 3. plastics :

- The intermolecular forces in these polymers are intermediate between those of elastomers and fibres.

- All plastics are polymers but all polymers are not plastics
- Plastic is a generic term often used to describe polymers that have plastic properties (i.e. they are able to moulded, shaped and formed relatively easily )

# On the basis of thermal processing behaviour, plastics may be classified in two groups.

**a) Thermo plastic**

**b) Thermo setting**

- **1. Thermoplastic Polymers:** Thermoplastics are polymers that soften on heating and become hard on cooling. These are the polymers in which intermolecular forces of attraction are moderate and there are no cross-links between the chains.

**E.g:** polyethylene, polypropylene, PVC, polystyrene , Poly tetra flouro ethylene (Teflon)  etc.

# Thermo Plastics properties

- These are linear or slightly branched molecules.
- polymers which are softened on heating and hardened on cooling
- Repeated heating or cooling do not alter any chemical change.
- These are prepared by addition/condensation polymerization.
- These are made of long chains attached by weak Vander wall’s forces of attraction.

- These are soft, weak and less brittle.
- These are reclaimed from waste.
- These solvable in some organic solvents.
- Resins and plastics are synononomous in this case.

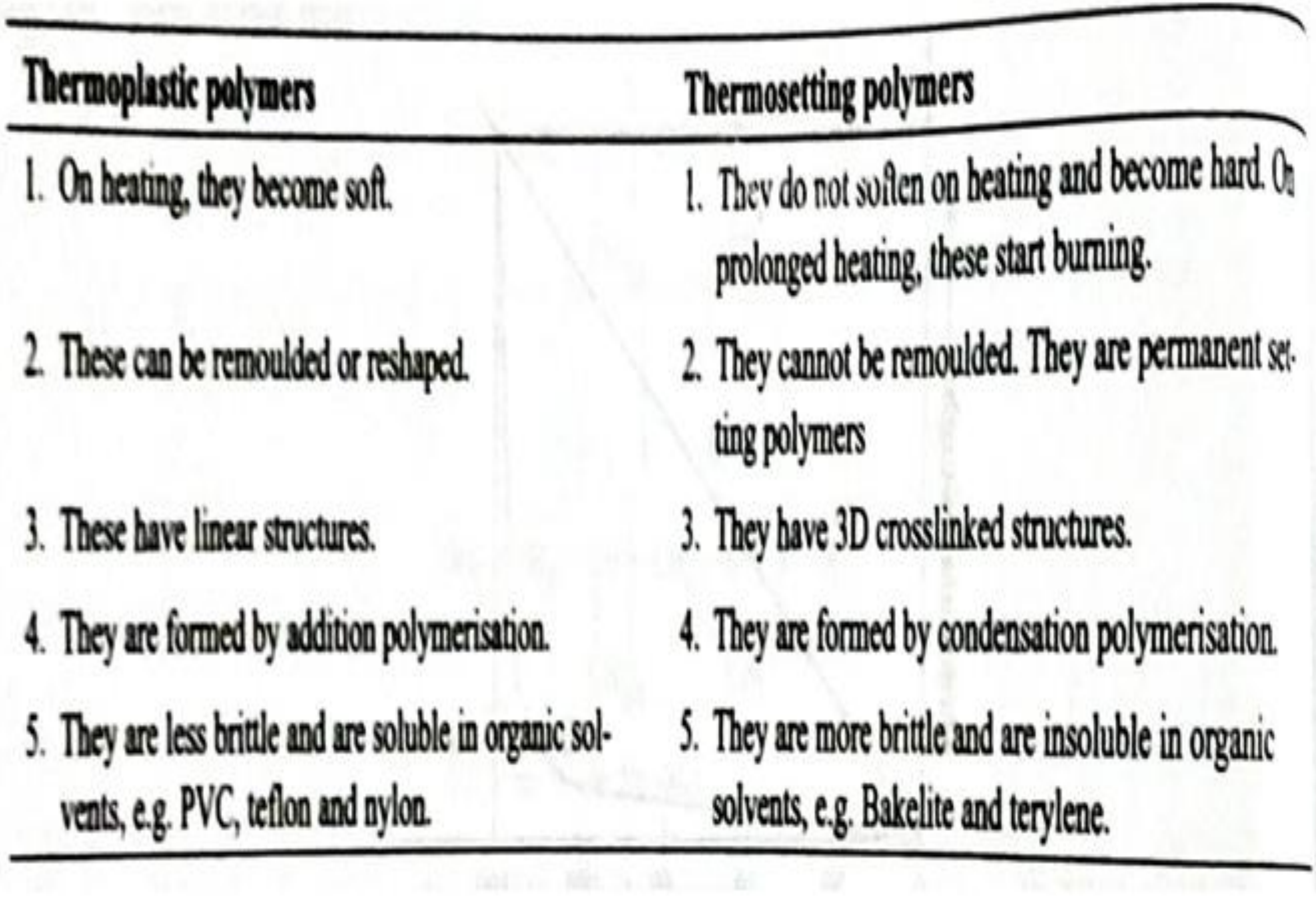
- **2. Thermosetting Polymers:** On heating, extensive cross-link is formed in these polymers between the polymeric chains and, thus, they become hard.

**E.g:** Bakelite , Novaloc , Terylene, silicons, nylon etc.

# 2.Thermo setting Resins

- The polymers which are hardened during their moulding process.
- Once they are hardened they cannot be softened. Hence these are called permanent setting resins.
- These acquire cross – linked, 3D, Network structure.
- The bonds retain their structure.

- Prolongated heating causes charring of the polymer.
- These are produced by condensation polymerization.
- These are hard, strong and more brittle.
- These cannot be reclaimed from waste.
- These are not soluble in organic solvents.



| Thermoplastic polymers | Thermosetting polymers |
|---|---|
| 1. On heating, they become soft. | 1. They do not soften on heating and become hard. On prolonged heating, these start burning. |
| 2. These can be remoulded or reshaped. | 2. They cannot be remoulded. They are permanent setting polymers |
| 3. These have linear structures. | 3. They have 3D crosslinked structures. |
| 4. They are formed by addition polymerisation. | 4. They are formed by condensation polymerisation. |
| 5. They are less brittle and are soluble in organic solvents, e.g. PVC, teflon and nylon. | 5. They are more brittle and are insoluble in organic solvents, e.g. Bakelite and terylene. |

# Preparation, properties & Engineering applications of polymers

# Polyvinyl Chloride(PVC)

- The monomer used for the manufacture of PVC is Vinyl chloride.

**Preparation:**

There are two ways of producing the monomer Vinyl chloride.

One method is by cracking ethylene dichloride in vapor phase at a temperature of 500$^{o}$C .

$$CH_2Cl\text{-}CH_2Cl \xrightarrow{500^{o}C} H2C=CHCl + HCl$$

The other method is by reacting acetylene with hydrogen chloride in presence of catalyst.

$$HCl + CH\Xi CH \xrightarrow[\text{catalyst}]{150^{o}C} H_2C=CHCl$$

Polyvinyl chloride is obtained by heating a water emulsion of vinyl chloride in presence of small amount of benzoyl peroxide or hydrogen peroxide in an autoclave under pressure.

$$H_2C=CHCl \xrightarrow{\text{polymerization}} ---[H_2C-CHCl--]_n$$

# Properties

PVC **is colorless, odorless** and **non-flammable.**

PVC is a poor conductor and a very good insulator.

PVC is very recyclable, more so than many other

PVC has a melting point at $160^0$C

PVC is highly fire resistant, it is widely used.

Has superior chemical resistance and high rigid

ity,  but is brittle.

PVC is a chemically inert and nonflammable powder having a high softening point of 148$^{o}$C.There are two kinds of PVC plastics

1. Plasticised PVC and
2. Rigid PVC

- Plasticised PVC is produced by mixing plasticisers like dibutyl pthalate, tricresyl phosphate etc., with PVC resin uniformly.

## Uses:-

Used for making rain coats,table cloths, curtains, coatings for electric wire and cables,toilet articles,tool handles, radio, T.V components,conveyer belts,pipes,bends,coupling valves etc.

- Rigid PVC or unplasticized PVC has high rigidity and high chemical inertness.

## Uses:-

It is mainly used for making sheets used to line big containers,tanks etc.Other materials like refrigerator components,tray,cycle and motor cycle mud guards, tubes,pipes etc are also manufactured out of unplasticised PVC.

# Polytetra fluoroethylene (Teflon)

Eg: $n\ F_2C{=}CF_2 \xrightarrow{\text{catalyst}} -(-CF_2-CF_2-)_n-$

**Tetra flouroethylene** **PTFE**

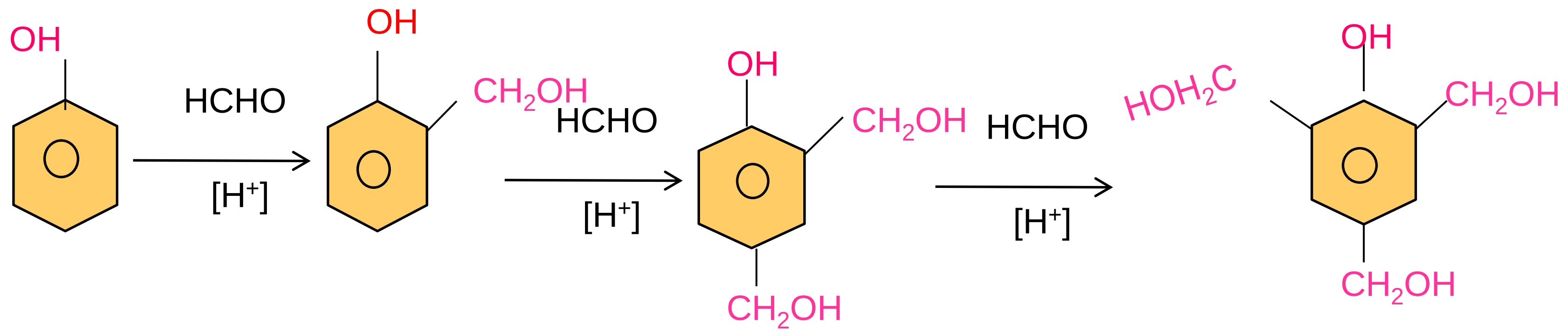
**Tetra flouroethylene Polymerizes at higher temperature and pressure in the presence of free radical initiators or catalysts like persulfate or hydrogen peroxide in aqueous media. Redox initiators such as ferrous sulphate and hydrogen peroxide can also be used.**

# Uses

- It is used to make insulation of motors,transformers,coils,capacitors
- Used to make self lubricating ball bearings.
- Teflon is used to make articles like pump valves, pipes, tanks etc.
- Used for storage chemicals.
- Teflon is the coating material used in non sticking frying pans as it is not wetted by oil or water.
- It is used in non-lubricating barings

# Bakelite (Phenol-formaldehyde resin)

- It is formed by condensation reaction of phenol & formaldehyde in presence of acid or alkali catalyst at proper temperature produces bakelite or phenol formaldehyde resin.
- Intial reactions of phenol & formaldehyde produces mono,di,tri-methylol phenols.



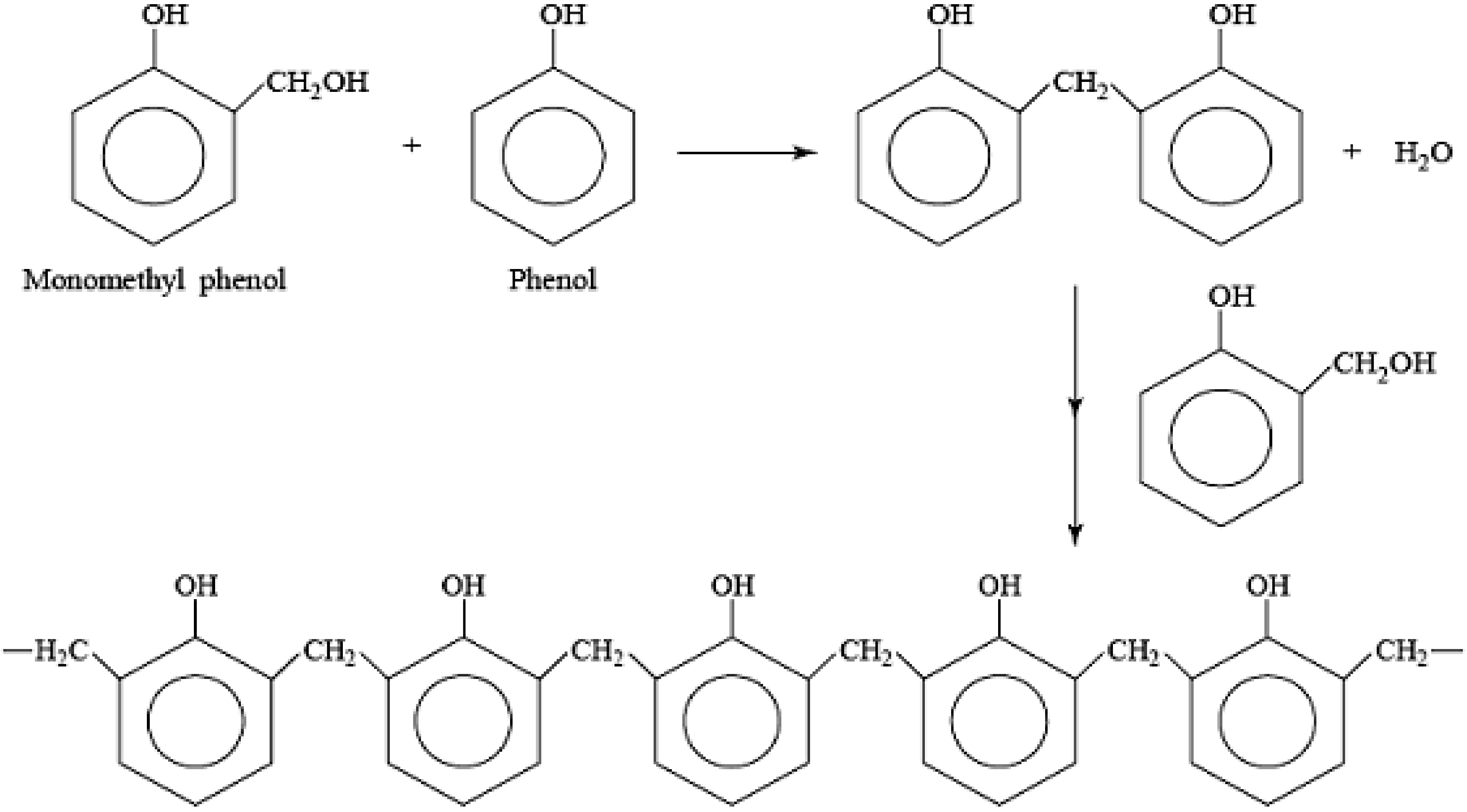
**Phenol**

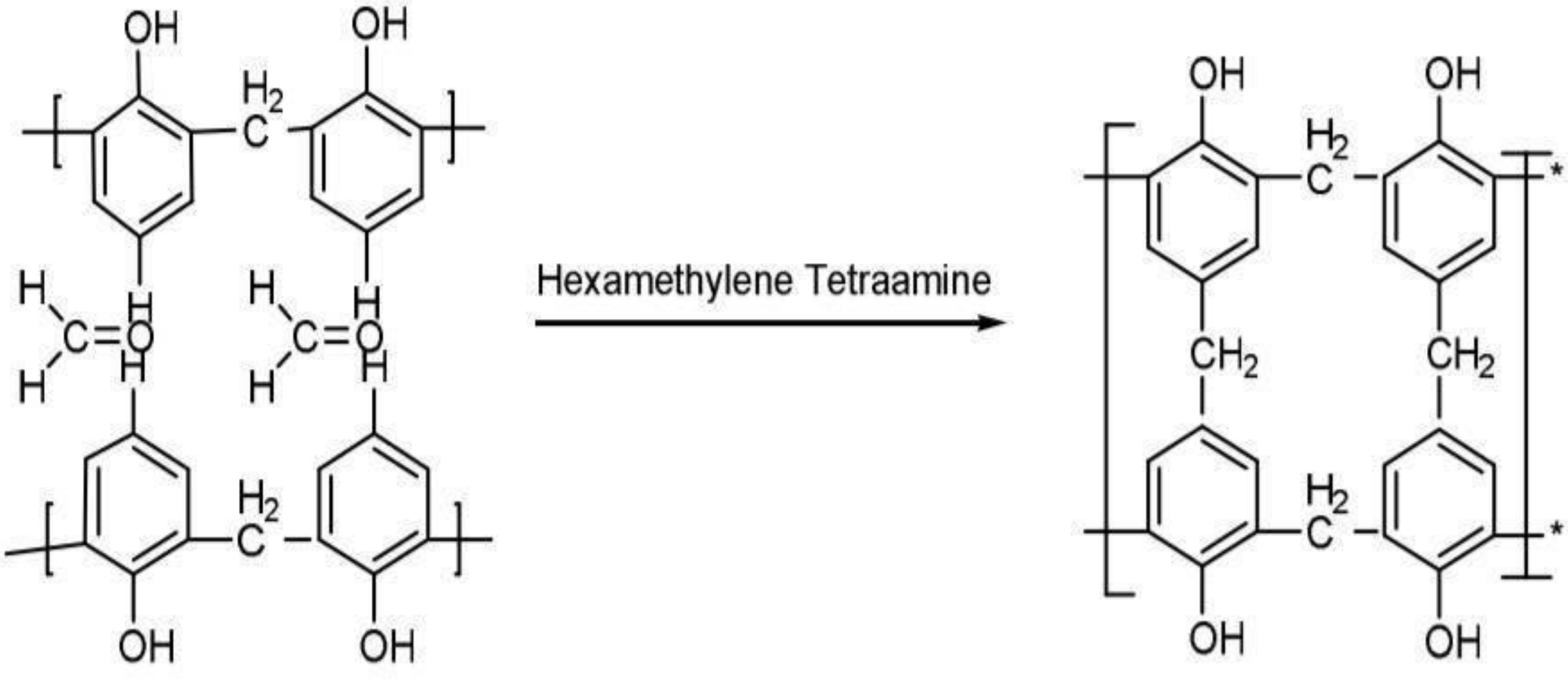
**Monomethylated phenol**

**Dimethylated phenol**

**Trimethylated phenol**

The monomethylated phenols condese with phenols to form low M.Wt linear polymers Known as **novolacs**. further heating of novolacs in the presence of hexamethylene tetramine yeilds **3-D cross linked** polymers known as **bakelites**. These are hard, rigid and infusible solid.

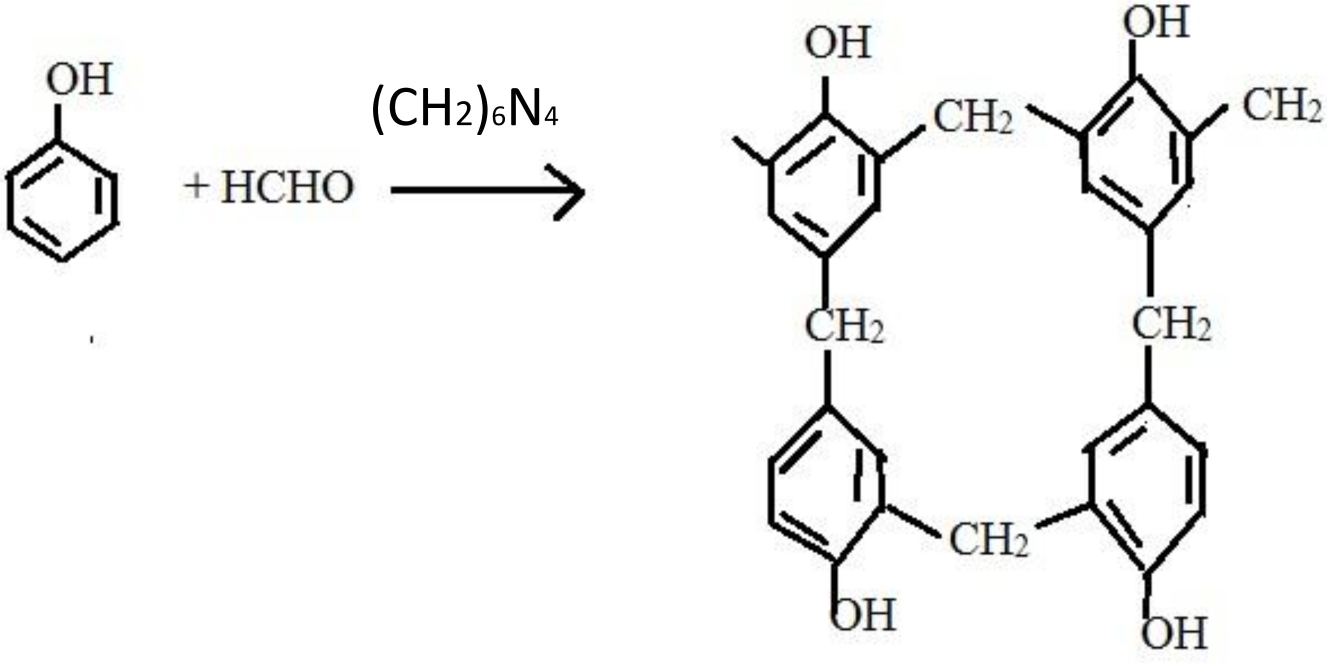

OH
CH2OH
Monomethyl phenol
+
OH
Phenol
OH
CH2
OH
+ H2O
OH
CH2OH
OH
OH
OH
OH
OH
—H2C
CH2
CH2
CH2
CH2
CH2—
Novolac



Novalac

Bakelite

OR



Bakelite

**Properties:**

- ✓ They are rigid, hard, scratch resistant, insoluble, water resistant .
- ✓ They posses excellent electrical insulating character.

**Uses:**

- ✓ For making electric insulator parts like switches, plugs, heater handles etc..,
- ✓ For impregnating fabrics, wood and other fillers for making decorative laminates and wall coverings for electrical parts including printed circuits.
- ✓ for production of ion-exchange resins
- ✓ Used in paints, varnishes and as adhesives

# Fibers

# Fabric

1. Fabric is made of fibers.
2. Types of fibers

**Synthetic**

Rayon

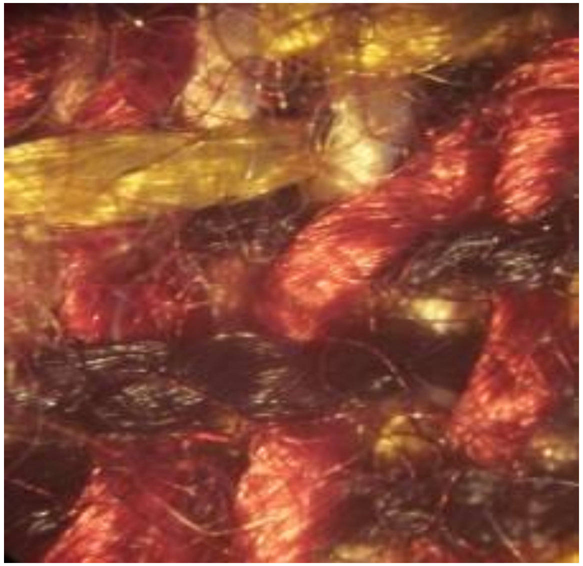
Nylon

Acetate

Acrylic

Spandex

Polyester



**Natural**

Silk

Cotton

Wool

Mohair

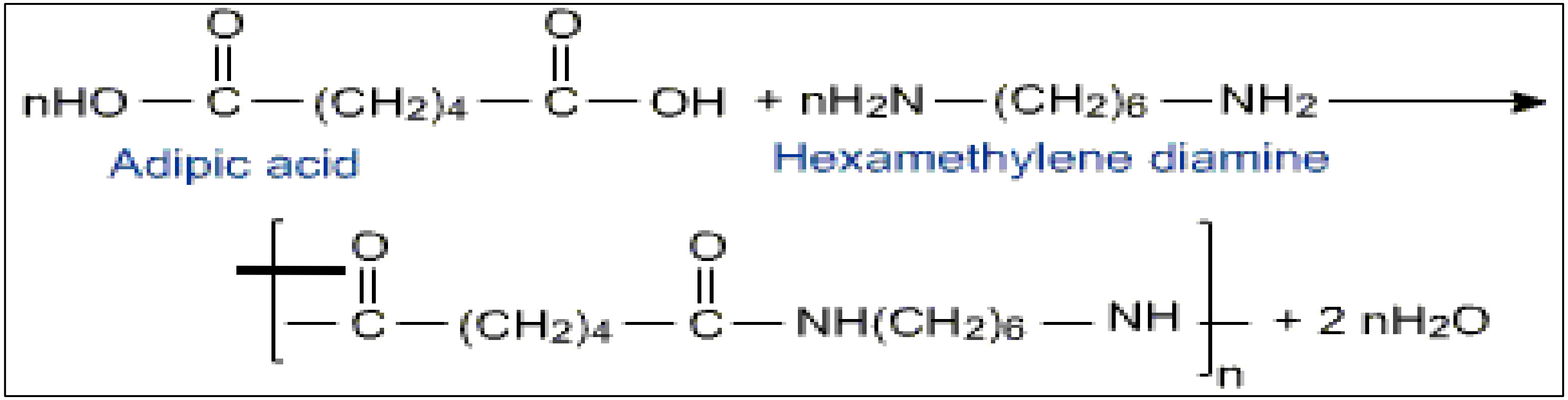
Cashmere

# POLYAMIDES

A polyamide is a polymer family that contains recurring amide groups of: R-CO-NH-R’ as integral parts of the main polymer compound.

## Nylon 6,6

- Nylon 6:6 is prepared by the condensation polymerization of adipic acid and hexamethylene diamine in the absence of air.



$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + nH_2N-(CH_2)_6-NH_2 \longrightarrow$$

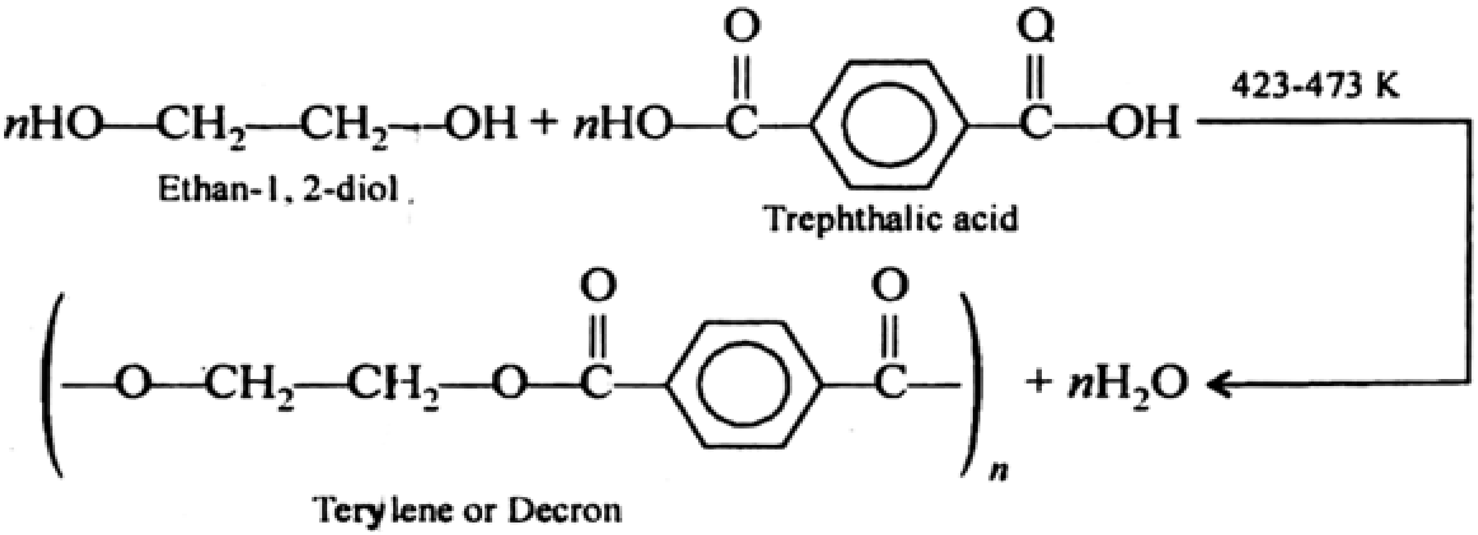
$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6-NH-\right]_n + 2\,nH_2O$$

## Properties and Uses

- ✓ It has remarkably low efficient of friction against many metals
- ✓ Self extinguishing when it comes in contact with a flame.
- ✓ Low water absorption and good strength which does not deteriorate even when used for a long period
- ✓ nyon 6:6 is used for making for fibers which are used for making socks, under garments, dresses, carpets.
- ✓ nylon 6:6 fiber has good dye wash fastness and UV light-fastness, and excellent performance in high-speed spinning processes.

# POLYESTER

- **Polyester** is a category of polymers which contain the ester functional group in their main chain.
- Ex:- Terylene



## Properties:

- Its properties include high tensile strength,
- high resistance to stretching, both wet and dry, and
- good resistance to degradation by chemical bleaches and to abrasion.

## Uses:

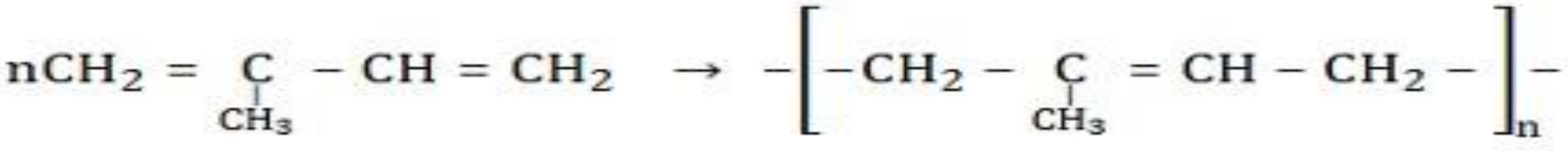
- The continuous filament yarn is used in curtains, dress fabrics , high-pressure fire hoses, men's shirts, and thread.
- The staple fiber is ideal for mixing with wool in men's and women's suits, as well as in dress fabrics, knitted wear, and washable woven sportswear, floppy disk, pillows ,furniture etc

# Rubber

- High polymers with elastic properties in excess of 300%.
- Is not straight chained but in form of a coil and stretched like a spring.

**Natural rubber**:

- Consist of a basic material latex which is a polymer of isoprene(2-methyl 1,3 butadiene).
- M.Wt is around 10,000 – 1,50,000



$$nCH_2 = \underset{CH_3}{\underset{|}{C}} - CH = CH_2 \rightarrow -\left[-CH_2 - \underset{CH_3}{\underset{|}{C}} = CH - CH_2 -\right]_n-$$

Isoprene

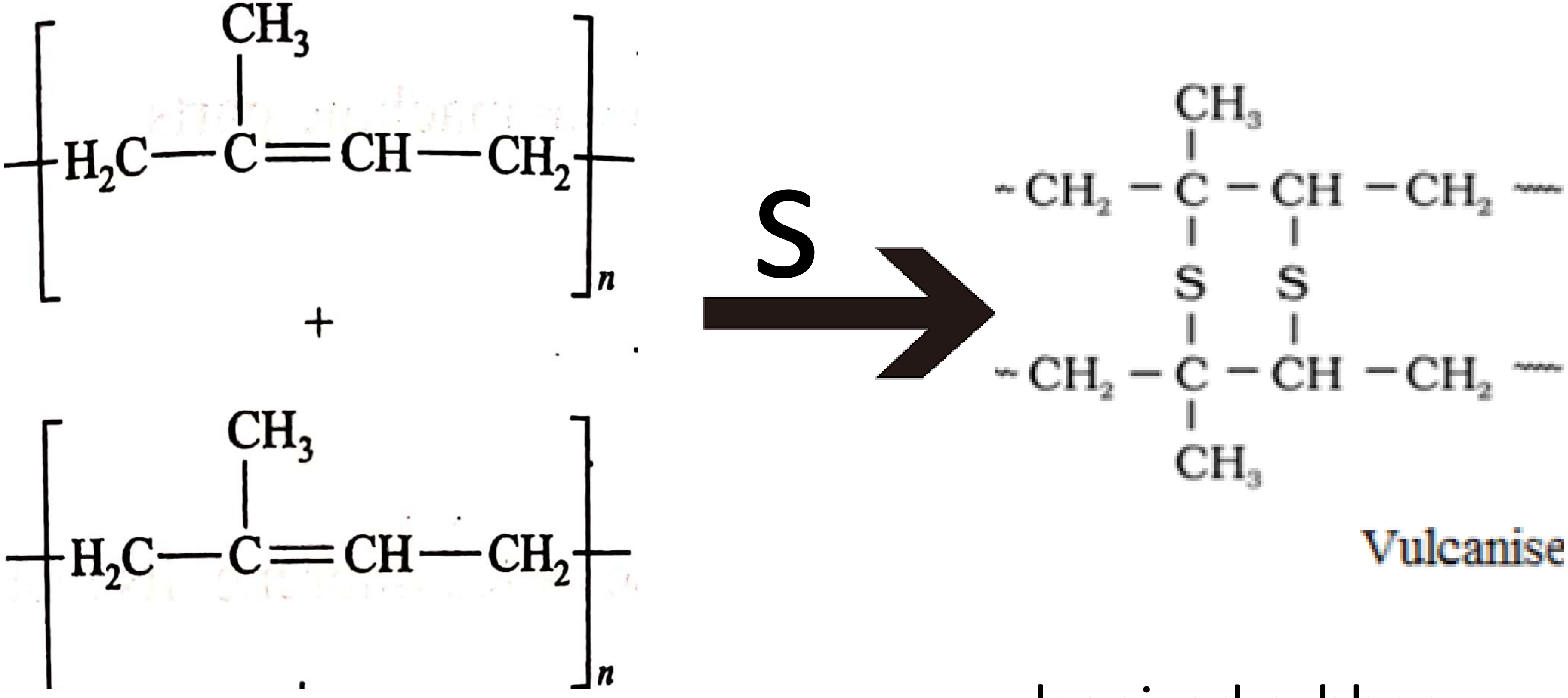
[2 – methyl butadiene]

Natural rubber

[Poly isoprene]

# Vulcanization:

- To improve the properties of rubber it is compounded with some chemicals like sulphur, $H_2S$, Benzoyl chloride etc. is called VULCANIZATION.
- The process consist in heating the raw rubber with sulphur at 100-140$^o$c.
- The sulphur is added on monomer double bonds.
- Thus serves to stiffen the material by a sort of anchoring and consequently, preventing inter molecular movement of rubber springs.
- Vulcanized rubber contains about 32% sulphur.



vulcanized rubber

# Properties of rubber improved by vulcanization:

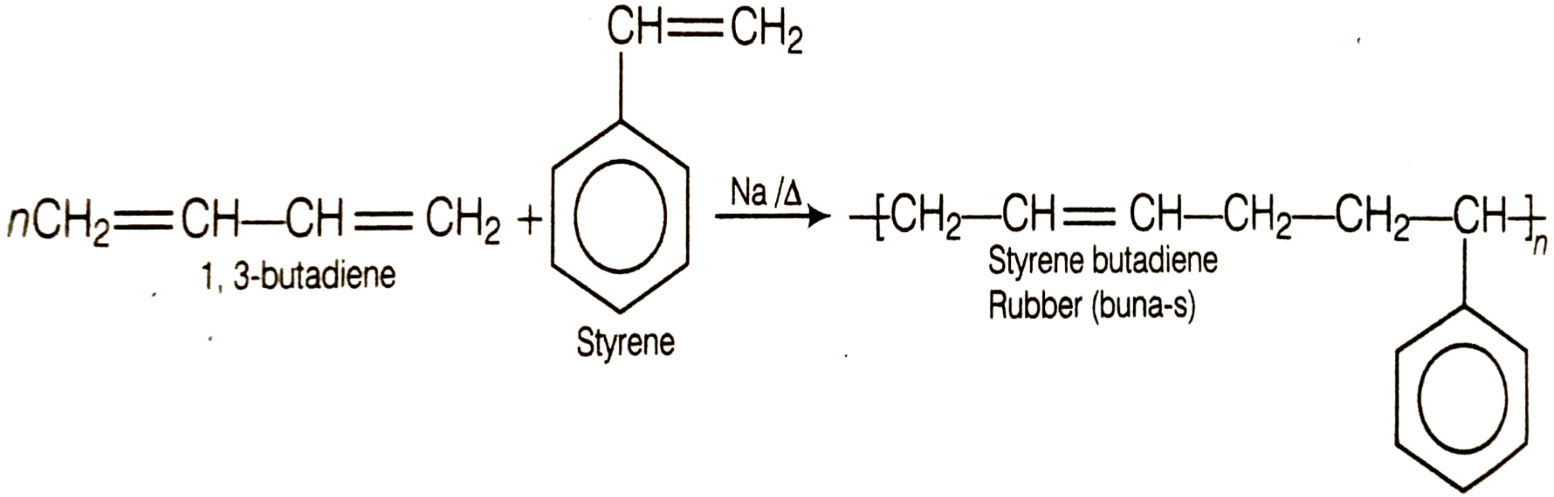
- ✓ tensile strength
- ✓ elasticity
- ✓ hardness
- ✓ tear strength
- ✓ abrasion resistance
- ✓ resistance to Solvents.

# ELASTOMERS:

- An elastomer / artificial rubber is any vulcanisable man made rubber like polymer, stretched to at least twice its length but it returns to its original shape and dimensions as

# BUNA-S

- ✓ BUNA-S is a copolymer of a mixture of 1,3- Butadiene and styrene in the ratio of 3:1 in the presence of sodium (which is polymerizing agent) gives styrene – butadiene copolymer (styrene – butadiene rubber) or BUNA –S.
- ✓ The name BUNA-S is made up of **Bu** which indicates 1, 3 – Butadiene, **NA** is for Sodium (Na) and S indicates Styrene.



## Properties of Buna-S

- ✓ It is very tough and a good substitute for natural rubber.
- ✓ It possesses high abrasion resistance.
- ✓ It has high load bearing capacity.

## Uses of Buna-S

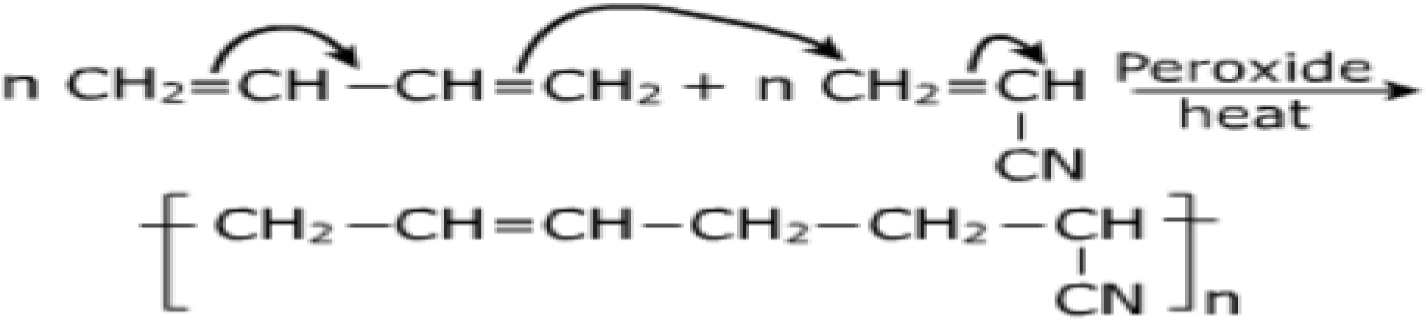
It is used for manufacturing automobile tyres.

It is used for making floor tiles, shoe soles,footwear components, tank linings,cable insulation etc.

# BUNA – N (Nitrile Rubber)

✓ BUNA-N is obtained by copolymerization of 1, 3 – Butadiene and acrylonitrile in presence of a peroxide catalyst.

✓ The name BUNA-N is made up of **Bu** which indicates 1, 3 – Butadiene, **NA** is for Sodium (Na) and **N** indicates acrylonitrile.



$$n\,CH_2{=}CH{-}CH{=}CH_2 + n\,CH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} \xrightarrow[\text{heat}]{\text{Peroxide}} \left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}\right]_n$$

Buna-N

## Properties of BUNA-N

BUNA-N is resistant to the action of petrol, lubricating oils and organic solvents

.

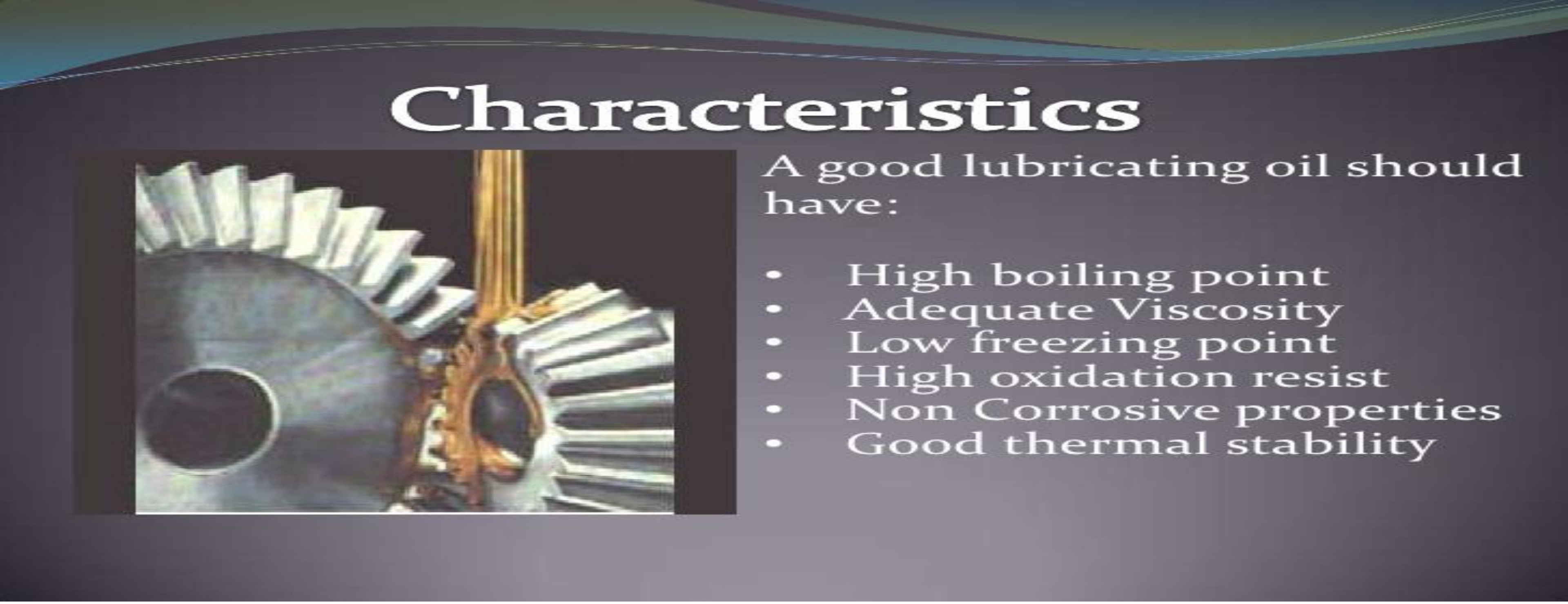
## Uses of BUNA-N

BUNA-N It is used in making oil seals, hoses, gaskets,,printing rollers,tank linings ,conveyor belts etc.

# LUBRICANTS

A **lubricant** is a substance, introduced to reduce friction between surfaces in mutual contact, which ultimately reduces the heat generated when the surfaces move.

**Lubrication** is the process or technique of using a lubricant to reduce friction in a contact between two surfaces.



# Characteristics

A good lubricating oil should have:

- High boiling point
- Adequate Viscosity
- Low freezing point
- High oxidation resist
- Non Corrosive properties
- Good thermal stability

## Functions of lubricants

1. Reduce friction
2. Prevent corrosion
3. Act as a coolant
4. Act as a seal
5. Prevent accumulation of dirt
6. Prevent  surface deformation

# Classification of Lubricants

- Liquid Lubricants
  - Eg.Mineral Oil, Petroleum Oil, Vegetable Oil etc
- Semi Solid Lubricants
  - Eg. Petroleum jellies
- Solid Lubricants
  - Eg. Graphite, Molybdenum Disulphide etc.

# Classification

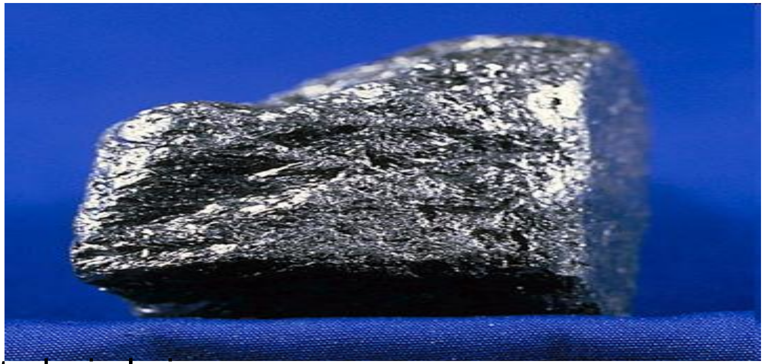
- **Liquid Lubricants:** Mineral Oil, Petroleum Oil, Vegetable Oil etc.

- **Semi Solid Lubricants:**

  Petroleum jellies

- **Solid Lubricants:**

  Graphite, MolybdenumDisulphide etc.

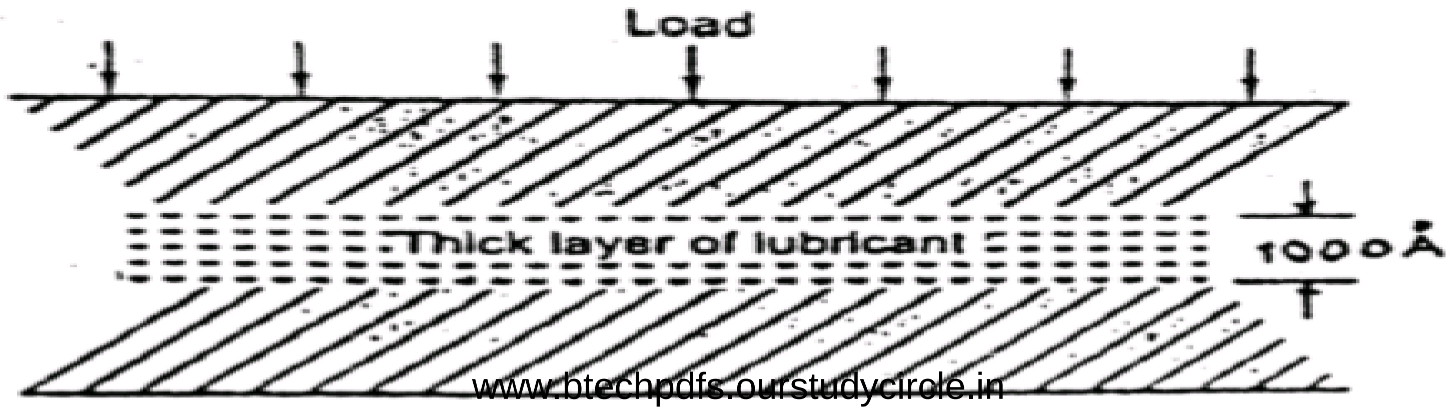


# Types Of Lubrications

- Thick Film or Fluid Film or hydrodynamic Lubrication
- Thin Film or Boundary Lubrication
- Extreme Pressure Lubrication

# 1.FLUID FILM, THICK FILM OR HYDRODYNAMIC LUBRICATION

1. In this method lubricant fills the irregularities of sliding surface and forms a thick layer ($1000A^0$) in between them and keep the material surface away from each other.
2. The lubricant should have minimum viscosity during working condition and it should remain inside and separate the surface.
3. This friction is quite common in the case of shaft running at a fair speed in a well lubricated bearing with moderate load.
4. This type of lubrication is done in delicate Instruments like watch, clock, guns, and sewing machines and in scientific instruments.
5. This type of lubrication is suitable for high speed ,low load machines



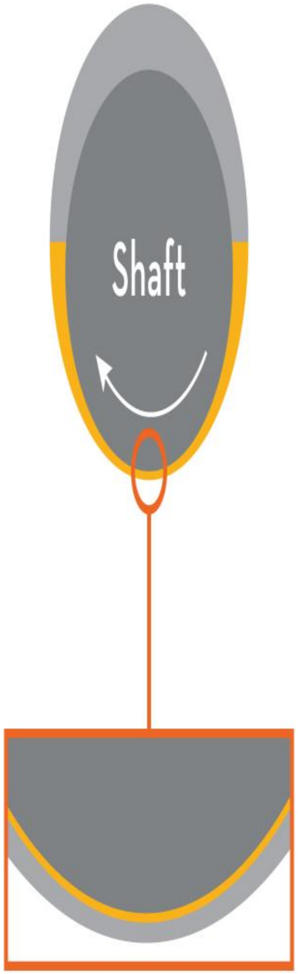
# OUNDARY LUBRICATION (OR)THIN FILM LUBRICATION:-

This type of lubrication is done when continuous film of lubricants cannot persist and direct metal to metal Contact is possible.

This will happen when:-

- Shaft starts moving
- Viscosity of oil is very low
- Speed is very low & Load is very high

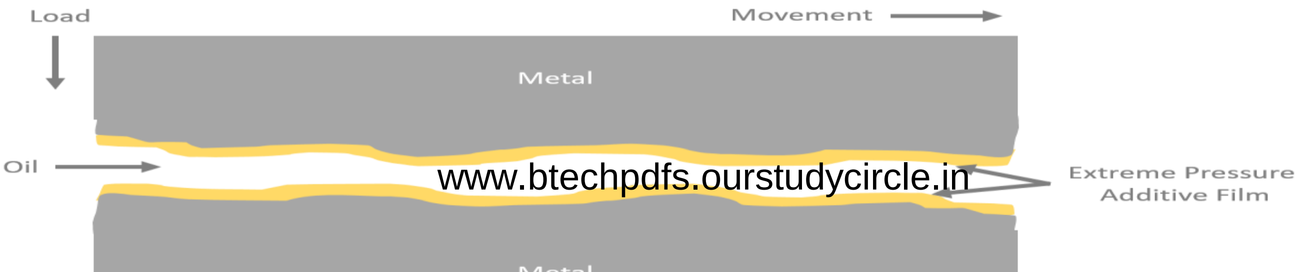
1. In this thin layer lubricant binds with the molecule of metal surface & can't be removed easily..
2. These adsorbed layers avoid direct metal to metal contact. Mineral oil, blended oil with some vegetable or animal oils are used for thin film lubrication.
3. Vegetable oil and their soaps have good property of adsorption but they break at high temp and mineral oil have of oiliness therefore blended oil is used for thin film lubrication.
4. This type of lubrication is suitable for low speed ,heavy load machine.
5. This type of lubrication employed in rollers and gear boxes.



Boundary Lubrication

# C. Extreme Pressure Lubrication

- When the surfaces under very high pressure, speed and a high local temperature is attained.
- So liquid lubricant fails to stick to the moving parts and may decompose and even vaporize.
- To meet this condition, special additives are added to the minerals oils, called “extreme pressure additives."
- These additives form on the metal surfaces more durable films capable of withstanding high loads and high temperature.
- Additives are chlorinated esters, sulphurised oils, tricresyl phosphates.
- Here the surface contact is continuous and extensive.
- The typical coefficient of friction is 0.05 to 0.20.
- This type of lubrication is suitable for high speed ,heavy load machines



# Properties of Lubricants

## 1. Viscosity

- It is a fluid's resistance to flow.
- Viscosity of the oil determines its performance under conditions.
- As oil heats up it becomes less viscous.
- Too low viscosity of oil >lubrication film can't maintained between the moving surfaces- excessive wear.
- Too high viscosity of the liquid> more friction.
- SIGNIFICANCE
- Viscosity helps in selection of lubricating oil
- Light oils generally used on parts moving at high speed under low load
- Heavy oils are used on parts moving at low speed under heavy load

# 2. Viscosity index

- The viscosity of lubricating oil changes with temperature is measured by a scale known as viscosity index
- e greater the V.I, the smaller the change in fluid viscosity for a given change in temperature, and vice versa.
- Thus, a fluid with a low viscosity index will experience a relatively large swing in viscosity as temperatures change.
- High-VI fluids, in contrast, are less affected by temperature changes.

# Determination of V.I

In the V.I scale the temperatures chosen arbitrarily for reference are $100^0$ and 210°F ($38^0$ and 99 °C).

A good lubricant should have high V.I

V.I of test oil is determined with help of two types of standard oils.

1. Pennsylvanian oil V.I is 100 at $100^0$ and 210°F
2. Gulf oil V.I is 0 at $100^0$ and 210°F .

## The V.I of the test oil is given by formula

$$\text{V.I} = \frac{L-u}{L-H} \times 100$$

**L= viscosity of low V.I oil(gulf oil V.I =0)**

**H=viscosity of high V.I oil(pennsylvanian oil V.I=100)**

**u= Viscosity of test oil at $100^0$ F**

# 3. Flash and Fire point

- The flash point of an oil is the lowest temperature at which it gives off vapours 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 vapours of the oil burn continuously even after the source of ignition is removed.
- These measurements are to assess the safety hazard of a lubricants with regard to its flammability.
- This is then used to warn of a risk and to enable the correct precautions to be taken when using, storing or transporting the liquid.

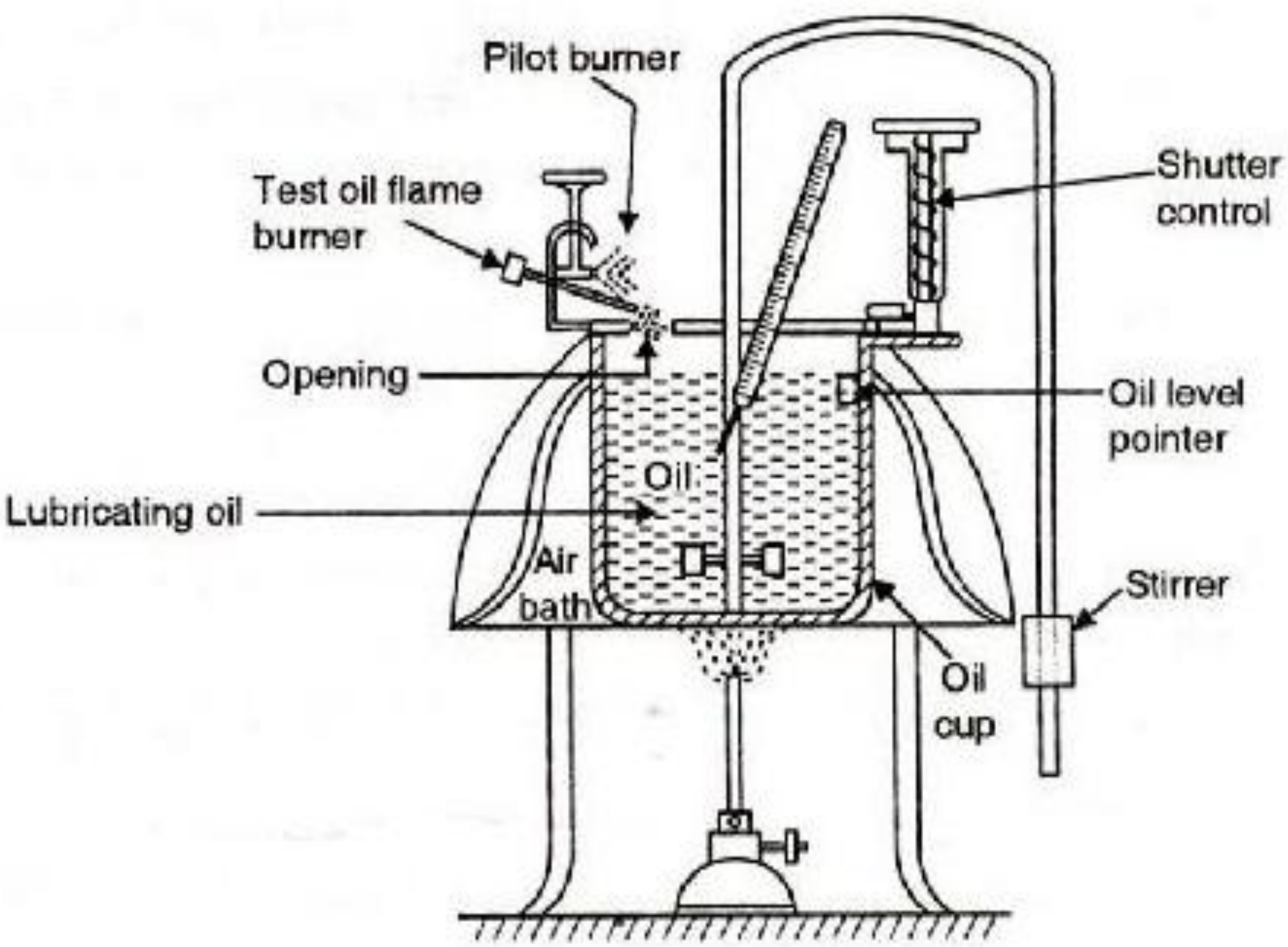
# Determination of Flash and Fire point

Pensky-Marten’s apparatus consists small oil cup. The cup is closed at the top with lid containing openings for inserting a thermometer ,stirrer and for introducing test flame.

**The procedure involves**

- Fill the oil cup with the oil to be tested up to the mark.
- Fix the cover on the top. The cover itself comprises the stirring device, the thermometer and the flame exposure device.
- Heat the apparatus by Bunsen burner slowly at the rate of $5^o$ to $6^o$ C per minute while the stirrer is rotated approximately 60 revolutions per minute.
- At every $1^0$ C rise in temperature, introduce the test flame for about 2 seconds into the oil vapour.
- The flash point is noted down when the test flame causes a flash in the interior of the cup
- Further heat the test oil at the rate of $1^0$C rise in temperature per minute.
- The temperature at which the vapours of the oil burn continuously for five seconds is recorded as the fire point of the oil.

# Flash and Fire Point



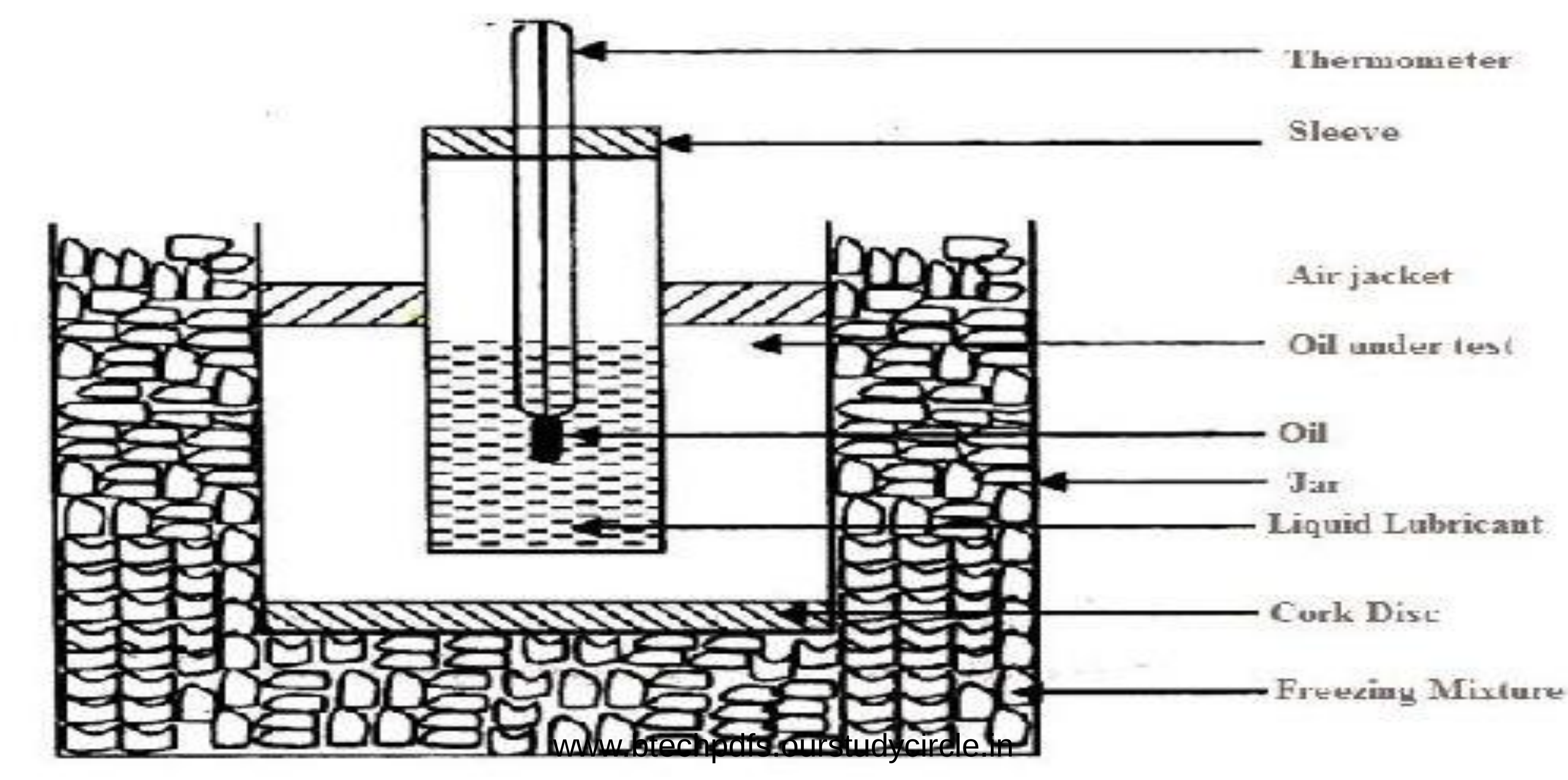
# Cloud and Pour Point

- Cloud point of an oil is the temperature at which the lubricant becomes cloudy or hazy when cooled.
- Pour point of an oil is the temperature at which the lubricant just cease to flow when cooled.
- Cloud point and pour points indicate the suitability of lubricants in cold conditions.
- Lubricants used in a machine working at low temperature should possess low cloud and pour points.

# Determination of Cloud and Pour Point

- The apparatus consists of a flat –bottomed tube enclosed in an air jacket.
- The air jacket is surrounded by freezing mixture contained in a jar.
- A sample of the lubricating oil is poured into a test jar and cooled in progressive steps.
- When inspection first reveals a distinct cloudiness at the bottom of the jar, the temperature recorded as cloud point.

- On further cooling in increments of 5$^0$F until no movement is observed at the surface of oil when the tube is held in a horizontal position for 5 seconds. This temperature is recorded as pour point.



# ACID VALUE OR NEUTRALIZATION NUMBER

It is the no. of mg of potassium hydroxide (KOH) required to neutralize free fatty acids in 1gr.of the oil

$$\text{ACID VALUE} = \frac{\text{Volume of KOH X Normality of KOH X Eq.wt of KOH}}{\text{Weight of oil sample}}$$

A good lubricating oil should possess acid value less than 0.1
Acid value greater than 0.1 oil is oxidized

## Applications of Lubricants

- Lubricants are primarily used to reduce friction stress between surfaces. They have the following uses:
- As anti wear, antioxidants, and antifoaming agents.
- As demulsifying and emulsifying agents.
- As rust and corrosion inhibitors.
- In machinery as engine oils, compressor oils, gear oils, and piston oils.
- As hydraulic brake and gear box fluids.
- Used in the soap and paint industries.
- Some specific uses of certain variants of lubricants are
- Synthetic lubricants are used in turbines, vacuum pumps, and semiconductor devices.
- Molybdenum is used as a paint pigment and as a catalyst.
- Liquid lubricants are used in medicines.