

UNIT – 4**“CEMENTS”****Introduction :-**

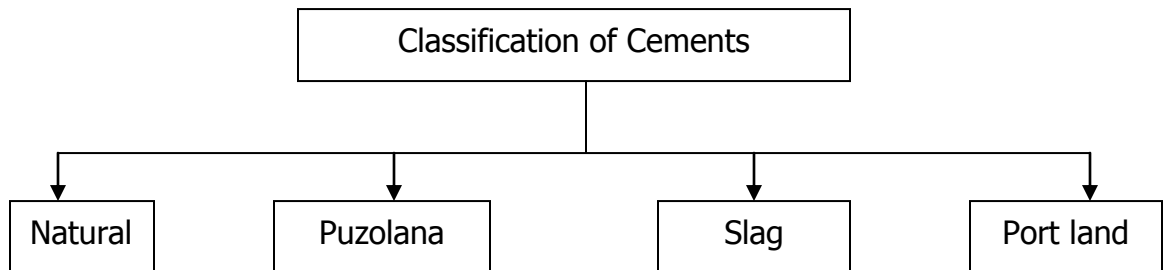
In this industrial age, the concrete is the most widely used non – metallic material of construction. It is used for the construction of buildings, bridges, high ways, dams, run – ways for the air craft etc.

Cement and its Classification :-

Cement is a material which possesses adhesive & cohesive properties and capable of binding materials like bricks, stones, building – blocks etc.

Classification of Cements :-

These are four types of cements viz. Natural, Puzzolana, Slag and Port land cement.

**(a) Natural Cement -****Preparation -**

- It is made by calcining a naturally occurring argillaceous lime – stone at a high temperature and subsequently, pulverizing the calcined mass.
- Calcium silicates and aluminates are formed by the combination of silica and alumina with calcium during calcination.

Properties -

- (i) It possesses hydraulic qualities.
- (ii) It is quite setting cement, and
- (iii) It possesses relatively low strength.

Applications -

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- (i) Mortars (combination of sand with natural cement) is used in laying bricks and setting stones.
- (ii) It is also used in large masses of concretes such as dams and foundations.

- (b) Puzzolana Cement** – It is oldest cement invented by Romans. It was used by them in making concrete for the construction of walls and dams.

Preparation –

- (i) This is made by mixing & grinding of natural puzzolana and slaked lime. Natural puzzolana is deposit of volcanic ash produced by rapid cooling of lava. Lava in turn is a molten mixture of silicates of calcium, iron & aluminium.

Puzzolana cements from hydraulic cementing materials.

Properties –

- (i) They also possess hydraulic properties.

Applications –

- (i) They are first mixed with portland cements and then used for different applications.

- (c) Slag Cement –**

Preparation –

- It is made from hydrated lime & blast furnace slag. A mixture of calcium and aluminium silicates (i.e., blast furnace slag) is granulated by pouring it into a stream of cold water.
- Subsequently, it is dried & mixed with hydrated lime. Then the mixture is pulverized to fine powder.
- Sometimes, accelerator like clay, salt or costive soda are added to hasten the hardening process.

Properties –

- (i) Slag cements are slow setting.
- (ii) They are poor in abrasion – resistance and
- (iii) They have lower strength.

Applications –

- (i) It is used for making concrete in bulk construction.

- (d) Portland Cement** – It is made by calcining (at about 1500°C) an intimate and properly proportioned mixture of clay and lime

containing raw materials. After calcination, retarder like gypsum is added.

Portland cement is also known as “magic powder”. It consists primarily of compounds of lime, silica alumina and iron. It forms a paste when mixed with water. This paste subsequently hardens and binds the aggregates (crushed rock, sand, gravel, etc.) together to form a hard durable mass called concrete. Thus, cement is one ingredient of concrete.

Portland cement is a type of cement, not a brand name. Each cement manufacturer makes Portland cement. All Portland cements are hydraulic cements because they set & harden under water.

Manufacture of Portland Cement –

- (i) **Raw Materials:-** Raw materials required for the manufacture of Portland cement may be divided into those:-
- (a) The lime (CaO) component (i.e. calcareous materials such as Aragonite, Calcite, Marl, Shale & Limestone).
 - (b) The silica (SiO₂) component (i.e. siliceous materials such as Clay, Marl, Shale & Sand).
 - (c) The alumina (Al₂O₃) component (i.e., Argillaceous materials such as alumina-ore refuse, clay, fly ash and shale).
 - (d) The iron (Fe₂O₃) component (i.e., ferriferous materials such as clay, iron, ore, mill scale etc.)

Manufacturing Process – The manufacturing of Portland cement involves the use of skills of engineers chemists & technicians to ensure & uniform product. The manufacturing involves the following operations:-

- (i) **Crushing :-** It is done in primary crusher (which reduces the size of limestone to an approx. 5-in) & in secondary crusher (it further reduces the size to $\frac{3}{4}$ - in).
- (ii) **Mixing :-** It begins with the acquisition of raw material such as limestone, sand & clay. These are mixed either by the dry process or by the wet process.
 - The dry process produces a fine ground powder. It is stored in bins.

- The wet process (in the presence of H₂O) results in a slurry, which is mixed & pumped to storage basins.
- (iii) **Burning** :- Both dry & wet processes feed rotary kilns where burning results in actual chemical changes.

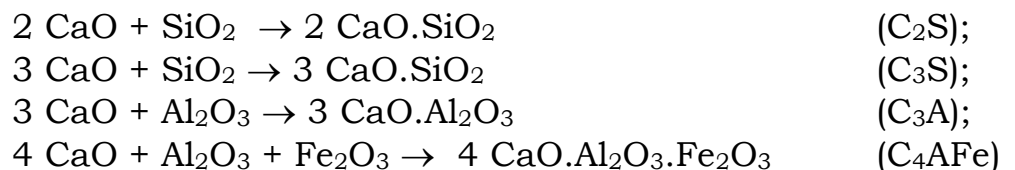
➤ There are different zone in the rotary kiln, viz.

(a) The drying Zone :- Here the temperature is moderate (100-500°C) and this zone is located at upper on fourth of the length of the kiln. This zone is known as drying zone, because the moisture is driven out & the materials get heated.

(b) Calcination Zone :- Its temp. is about 1000°C & it is the middle portion of the kiln. In this zone, CO₂ is expelled from lime-stone, quick lime (CaO) is formed in the form of small lumps, called nodules.



(c) Burning Zone :- Its temperature is about 1400-1500°C and is the bottom and hottest portion of the kiln. In this zone, mixture melts & forms little rounded pasty masses of about the size of the peas which are called clinkers. The clinkers product is greenish black or black in colour & has rough textured. In this zone, lime & clay undergo fusion forming calcium aluminates & silicates via:



(d) Grinding Zone :- From clinker storage the material is transported to final grinding where it is ground to the requisite fineness according to the class of the product. Finely ground clinker sets very fast by absorption of moisture from the atmosphere.

- To control the setting time of the Portland cement (when it is mixed with water) approx 2 to 3% gypsum (CaSO₄·2H₂O) is added.

The mixture of clinker & gypsum powder is known as Portland cement. It is stored in silos from which it is bagged or loaded for shipment.

Flow chart

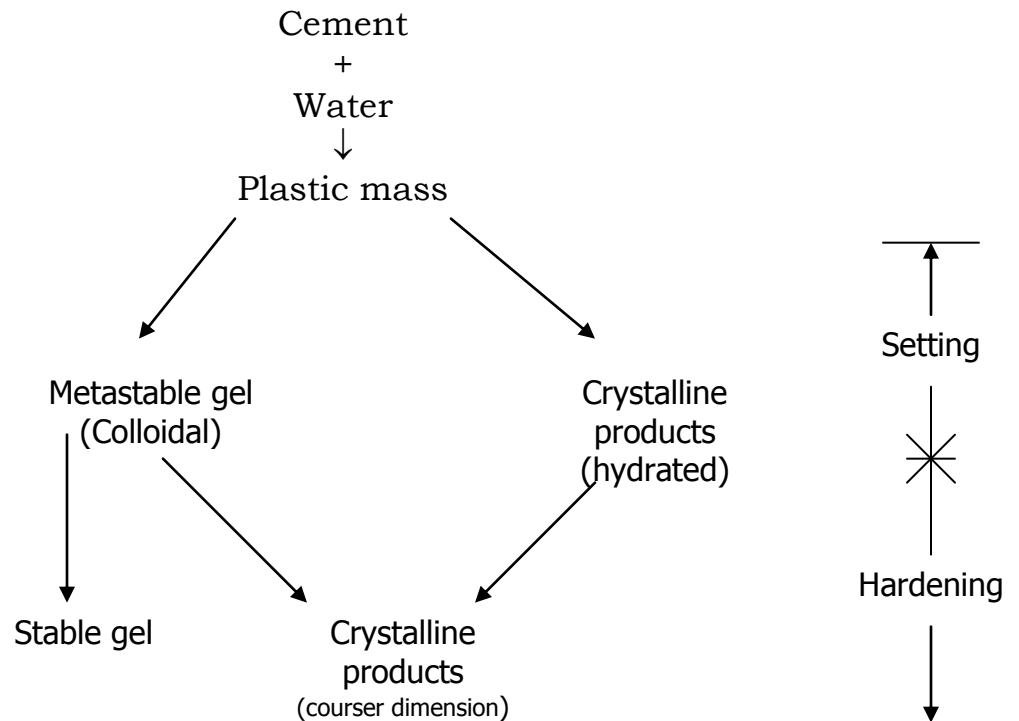
Pros and Cos of dry and wet process

	Dry Process		Wet Process
1.	It is a slow and costly process.	1.	It is comparatively faster and cheaper process
2.	Cost of production of cement is less, as the fuel consumption is low. Shorter kiln is sufficient.	2.	Cost of production is somewhat higher because of the higher fuel consumption. As longer kiln is needed to drive off the excess H ₂ O.
3.	The quality of cement produced is inferior.	3.	The quality of cement produced is somewhat superior, as more accurate control of composition can be attained.
4.	This process is adopted when the raw materials are quite hard.	4.	This process is preferred when the raw materials are soft.
5.	The process is not suitable when the principal raw material has an inherent moisture content of 15% or more, as it is uneconomical to drive away the excessive quantity of moisture.	5.	This process has to be adopted in this case.

Setting and Hardening of Cement -

When water is mixed with cement paste to form a fluid paste, hydration of cement takes place. The mixture eventually becomes stiff and then hard. This process is known as setting. After hydration, unhydrated compounds become hydrated which have less solubility. Hence they are precipitated as insoluble salts or crystals. These have the ability to surround sand, crushed stones or other inert materials & bind them very strongly.

The physical changes occurring in the setting and hardening of cement may be summarized diagrammatically as follows.



Schematic diagram of setting and hardening of cement

Hardening of cement can be explained on the basis of two theories.

- (i) **Colloidal Theory (by Michaelis)** :- According to this theory, during hydration silicate gels are formed which undergo hardening and are responsible for the hardening of cement.
- (ii) **Crystalline Theory (by Lechatties)** :- According to this theory, constitutional compounds after hydration form crystalline products. These crystalline products undergo interlocking which is responsible for hardening of cement.

Thus, it can be concluded that setting & hardening of cement is due to the formation of interlocking crystals reinforced by the rigid gels formed by the hydration & hydrolysis of the constitutional compounds.

Stiffening of a concrete mixture with little evidence of significant heat generation is known as false set. Further mixing without additional water can restore plasticity in such cases.

In some cases, cement also exhibits a flash set. In these cases the cement has hydrated & further remixing will do not good.

- (iii) Chemical composition of Portland Cement :-** Portland cements are composed of following four basic chemical compounds.

S.No.	Name	Chemical Formula	Abbreviation
01	Tricalcium Silicate	3 CaO SiO ₂	C ₃ S
02	Dicalcium Silicate	2 CaO SiO ₂	C ₂ S
03	Tricalcium Aluminate	3 CaO Al ₂ O ₃	C ₃ A
04	Tetracalcium Alumino-ferrite	4 CaO Al ₂ O ₃ Fe ₂ O ₃	C ₄ AFe

- (iv) I. S. I. Specifications of Portland Cement:-** Specifications for ordinary Portland cement as per Indian Standard : 269 – 1975, are given below :

- (i) Lime saturation factor $\left[\frac{\text{CaO} - 0.7\text{SO}_3}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3} \right] = 0.66 \text{ to } 1.02.$
- (ii) The ratio $\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$ Shall not be less than 0.66
- (iii) Insoluble residue should not exceed 2%.
- (iv) The weight of magnesia (MgO): Should not exceed 6%.
- (v) Total sulphur contents, calculated as sulphuric anhydride (SO₃) shall not be more than 2.75%.
- (vi) Loss on ignition shall not exceed 4%.
- (vii) Fineness not to exceed 10% after sieving the residue (by weight) on B. S. 170 – mesh test sieve.
- (viii) Setting times : Initial = 30 minutes., Final = 10 Hours.
- (ix) Heat of hydration :
- | | | |
|-------------------------|---|---------------|
| After seven days | : | ≤ 65 cal/ gm. |
| After twenty eight days | : | ≤ 75 cal/ gm. |
- (x) Compressive strength :
- | | | |
|------------------|---|---------------------|
| After three days | : | ≥ 1600 Ib/sq. inch. |
| After seven days | : | ≥ 2500 Ib/sq. inch. |
- (xi) Tensile strength :
- | | | |
|------------------|---|--------------------|
| After three days | : | ≥ 300 Ib/sq. inch. |
| After seven days | : | ≥ 375 Ib/sq. inch. |

(v) Physical Properties of Portland Cement:

- (i) Fineness : -**

- It affects the hydration of cement.
- For a given weight of cement the surface area of the grains of a fine ground cement is greater than for a coarse – ground cement.
- Hence, hydration process occurs more rapidly in a fine ground cement as water is in contact with more surface area.
- The cement should not be ground too finely because there is a possibility of prehydration due to accidental contact with moisture vapour during manufacturing & storage.
- This results in loss in cementing properties of the material.
- In general, the finer a cement is ground the higher the heat of hydration & resulting accelerated strength gain.

(ii) Soundness :-

- It is the ability of a cement to maintain a stable volume after setting.
- A sound cement resists cracking, disruption & eventual disintegration of the material mass.
- An unsound cement has excessive amounts of free lime which is enclosed in cement particles.
- After the cement has set, when the moisture reaches the lime, lime expands with considerable force, disrupting the set cement.

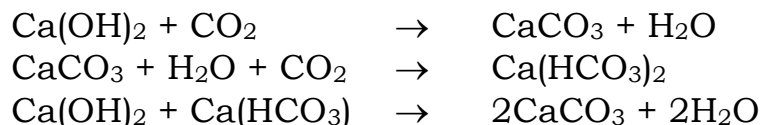
(vi) Decay of Cement :-

The cement constituents are susceptible to attack by salty water & other acidic solutions.

- Acidic water can attack the cement structures. With decrease of pH (on increase of acidity), the rate of attack increases. Dissolved CO₂ or presence of other organic & inorganic acids are responsible for acidity of water.

Decay of cement is due to

- (a) The leaching out of free lime from it. This leaching is due to the chemical action of CO₂ in acidic water.



Initially, insoluble CaCO₃ is formed, which is then dissolved out with further reaction with CO₂ & H₂O leading to the formation of soluble Ca(HCO₃)₂ calcium bicarbonate. Till there is consumption of all CO₂, this cycle of reaction is continuous.

- (b) Hydrolysis of silicates & aluminates, which will also be dissolved out.

Prevention :- Decay of cement can be minimized by coating the surface with epoxy resin paint or bituminous or linseed oil (or other drying oils). This coating makes the surface impermeable to acidic H_2O .

“LUBRICANTS”

INTRODUCTION:-

In all types of machines, the surface of moving, sliding or rolling parts rub against each other. This mutual rubbing of one part against another generates frictional force which offers resistance to the relative motion of these surfaces. Friction also generates heat which gets dissipated thereby causing loss in the efficiency of the machine.

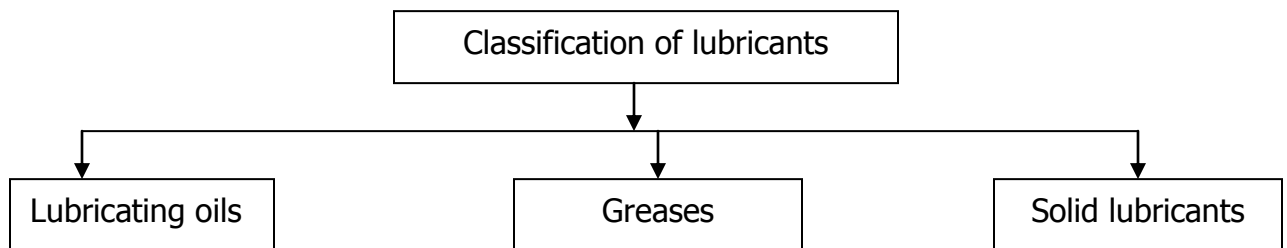
These drawbacks of frictional resistance can be minimized by applying a thin layer of certain substances, known as lubricant in between the moving/sliding/rolling surfaces.

- A lubricant may thus be defined as a substance which reduces the friction when introduced between two surfaces & the phenomenon is known as lubrication.

Functions of Lubricants :-

- (i) The first and foremost function of a lubricant is to reduce friction.
- (ii) It reduces wear, tear & surface deformation.
- (iii) It acts as coolant to carry away heat.
- (iv) It keeps out dirt.
- (v) Sometimes, it acts as a seal.
- (vi) It reduces the maintenance & running cost of the machine as it prevents rust & corrosion.
- (vii) It transmits fluid power.
- (viii) It also reduces loss of energy in the form of heat.

Classification of Lubricants :-



On the basis of their physical state, lubricants can be classified as:

- (i) Lubricating oils (or liquid lubricants).
- (ii) Greases (or semi – solid lubricants); and
- (iii) Solid lubricants.

(1) Lubricating Oils :- Lubricating oils are also known as liquid lubricants and are further classified into three categories viz. Animal & Vegetable oils, Mineral or Petroleum oils and Blended oils.

Characteristics of good Lubricating Oils : -

- High boiling point.
- Low freezing point.
- Adequate viscosity for proper functioning in service.
- High resistance to oxidation & heat, non- corrosive properties and stability to decomposition at the operating temperatures.

Functions of Lubricating Oils:-

- Lubricating oils provide a continuous fluid film in between moving/sliding/rolling surfaces & reduce friction, wear & heat generation.
- They also act as cooling & sealing agent.
- They also prevent corrosion.

Types of Lubricating Oils are briefly described below:-

(a) Animal & Vegetable Oils:- Animal & vegetable oils possess good “oiliness” & hence they stick to the surface of machine parts, even under high temperatures & heavy loads.

	Lubricating Oils	Uses
I	Animal Oils	
	Lard Oil	For lubricating ordinary machine parts
	Neats Foot Oils	For lubricating clocks & sewing machines particularly suitable for light machinery.
	Sperm Oil	Particularly suitable for light machinery.
II	Vegetable Oils	
	Caster Oil	Very good lubricant for bearing and machinery operating at high speeds & low pressures like racing cars.
	Palm Oil	For lubricating delicate instruments such as scientific equipment.

Animal and vegetable oils have very limited uses at present because they are costly have less resistance to oxidation & after oxidation form gummy and acidic products. They get thickened on coming in contact with air. When allowed to remain in contact with humidity or moisture they show some tendency to hydrolyze.

Actually these oils are used as blending agent for mineral oils so as to produce, desired effects in the latter.

(b) Mineral or Petroleum Oils:- These are basically lower molecular weight hydrocarbons with about 12 to 50 carbon atoms. Their viscosity increases with the length of the hydrocarbon chain. They are obtained by distillation of petroleum.

- As they are cheap, available in abundance & stable under service conditions, hence they are widely used.
- In comparison to animal and vegetable oils, oiliness of mineral oils is less.
- The addition of higher molecular weight compounds like oleic acid and stearic acid, increases the oiliness of mineral oil.

(c) Blended Oils:- Desirable characteristics of lubricating oils can be improved by adding small quantities of various additives. The oil thus obtained are known as blended oils or compounded oils.

Various additives, their purpose functions & typical examples are summarized below:

(i) Lubricant Protective Additives:-

	Additive Type	Purpose	Functions	Typical Examples
1.	Antioxidant	Retard oxidative decomposition	Terminate free radical chain reactions and Decompose peroxides	Aromatic amines, Hindered Phenols etc.
2.	Metal Deactivator	Decrease catalytic effect of metals on	By complexing with metal ions, they form	Amines, Sulphides or Phosphites

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		oxidative rate	inactive layer on metal surfaces	etc.
3.	Antifoamant	Prevent persistent foam formation by lubricant	Speed collapse of foam by reducing surface tension	Silicon, Polymers

(ii) Surface Protection Additives:-

	Additive Type	Purpose	Functions	Typical Examples
1.	Rust and Corrosion inhibitor	Prevent rusting and corrosion of metal parts in contact with the lubricant	Neutralisation of corrosive acids and preferential adsorption of polar constituent on metal surface to provide a protective film.	Metal phenolates, basic metal sulfonates, fatty acids and amines.
2.	Anti wear and EP agent	Reduce friction and wear and prevent scoring and seizure	Prevent metal to metal contact by chemical reaction with metal surfaces to form a film with lower shear strength than the metal	Zinc dithiophosphates, organic phosphates & acid phosphates, sulfurized fats etc.
3.	Friction modifier	Change coefficient of friction	Preferential adsorption of surface active materials	High molecular wt. or genie phosphorus & phosphoric acid esters organic fatty acids & amines
4.	Detergent	Keep surfaces deposits free	Neutralize the sludge & varnish precursors and keep them soluble	Magnesium phenolates, phosphates & suffocates
5.	Dispersant	Keep insoluble contaminants dispersed in the lubricant	Prevent agglomeration of contaminants as they are bonded by polar attraction to dispersant molecules contaminants are kept in suspension due to solubility of	Alkyl succinimides, polymeric alkyl thiophosphonates.

			dispersant.	
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(iii) Performance Additives:-

	Additive Type	Purpose	Functions	Typical Examples
1.	Viscosity modifier	Reduce the rate of viscosity change with temperature	Polymer expand with increasing temperature to counteract oil thinning	Polymers & co-polymers of olefins, alkylated styrenes, methacrylates & butadiene.
2.	Pour point depressant	Enable lubricant to flow at low temperature	Reduce interlocking by modifying wax crystal formation	Polymethacrylates, phenolic polymers & alkylated naphthalene.
3.	Seal swell agent	Cause swelling of elastomer by chemical reaction		

(2) Greases or Semi – Solid Lubricants :- A semi – solid lubricant obtained by combining lubricating oil with thickening agent is termed as “Grease”.

- Shear or frictional resistance of Greases is much higher than oils hence they can support much heavier load at lower speed.
- Coefficient of friction of greases is much higher than that of lubricating oils. Therefore, whenever possible, it is better to use an oil instead of grease.
- Compared to lubricating oils, greases cannot effectively dissipate heat from the bearing.
- That’s why the grease lubricated bearing works at relatively lower temperatures as compared to the oil – lubricated bearing.

Preparation :- Grease are made by saponification of fat with alkali followed by adding hot lubricating oils with constant mixing.

- Consistency of the finished greases is governed by the total amount of the mineral oil.

Applications :- Greases have the following uses:-

- In rail axle boxes.
- In bearings & gears that works at high temperatures.
- In machines preparing paper, textiles, edible articles etc. where dripping of oils is undesirable.
- In situations where bearing needs to be sealed against entry of dust, darts grit or moisture, as the greases are more resistant to contamination by these agents.

Classification of greases on the basis of the soap used in their manufacture

- (i) Soda – based greases** employ sodium soaps as thickening agent in petroleum oils. As the sodium soap content is soluble in water so these greases are not water resistant.
 - These greases can be used up to 175°C.
 - They are suitable for use in ball bearings which generates frictional heat.
- (ii) Lithium – based greases** employ lithium soaps as thickening agent in petroleum oils.
 - These greases are resistant to water & have good high – temperature properties.
 - These greases are stable in storage, have high mechanical & oxidation stability.
 - They have high melting point (about 150°C).
- (iii) Calcium – based greases** employ calcium soaps as thickening agents in petroleum oils.
 - These greases are also known as cap greases. These greases are the cheapest & most commonly used.
 - These greases are suitable for lubricating caterpillar treads, tractors, water pumps etc.
- (iv) Axle greases** are very cheap resin greases. They are prepared by adding lime to resin & fatty oils. After thorough mixing & standing staff mass greases floats out. Talc, mica any other suitable filter is also added to them.
 - They are resistant to water & used fro equipment working at low speeds & high loads.

- (3) Solid Lubricants :-** These lubricants reduce friction by separating two moving surfaces under boundary conditions. They are used either in the dry powder form or mixed with oil or water.

Solid lubricants find applications in :-

- (i)** Commutator bushes of motors and electronic generators where contamination of grease or lubricating oil is unacceptable.
- (ii)** Internal combustion engines where a tight film is desired between the piston rings & the cylinder for increasing compression.
- (iii)** In this application, combustible lubricants must be avoided.
- (iv)** Lubricating film cannot be secured by using lubricating oils or greases because of the high operating temperatures.

The two most commonly used solid lubricants are :-

- (i) Graphite:-** Graphite consists of number of flat plates made up of network of hexagons in which each carbon is in sp^2 hybridization state (Fig. 1(a)).
 - The plates are separated from each other by $4A^0$ & are held together by weak Vander Wall's forces so that even a small force is sufficient to slide the layers parallel to each other. Hence, it has low coefficient of friction.

Figure 1 (a)

Properties:-

- It is very soapy to touch, non – inflammable & not oxidized in air below $375^{\circ}C$.

Uses :-

- It is used in the powdered form or as suspension in oil or water along with tannin as emulsifying agent.
- Graphite dispersed in water is useful where a lubricant free from oil is needed.

- Graphite greases is useful for higher temperature applications.
- Graphite dispersed in water is used in internal combustion engines as it gives a tight – fit contact by forming a film between the piston rings & the cylinder thereby increasing compression.

(ii) Molybdenum Disulphide :- It was a sand witch like structure in which a layer of molybdenum atoms lies between two layers of sulfur, which are 6.26\AA a part; see fig. 1(b).

Figure 1(b)

Properties:-

- MoS₂ has low shear strength in a direction parallel to the layers due to poor interlaminar attraction. That's why MoS₂ has very low.
- It is stable in air upto 400°C.

Uses :-

- A solid – film lubricating surface useful for space vehicles is made from (70% MoS₂ + 7% graphite) bonded with 23% silicates, which can withstand extreme temperatures, low pressure and nuclear radiation.

(4) Synthetic Lubricants :- These are manufactured or synthesized in chemical plants or refineries to produce tailor made products that can lubricate like conventional lubricants but at severe or extreme condition as they exhibit unique combinations of properties like high temperature stability, extended temperature range, long service life even in reactive environments etc.

Relative properties of synthetic lubricants after incorporating additives are summarized below :-

Synthetic lubricants	Low temp. properties	High temp. stability	Viscosity index	Lubricity	Volatility	Fire resistance	Hydrolytic stability
Polyalpha-olefines (PA ^o)	G	G	G	G	G	P	E
Diesters	E	E	V	G	A	F	F
Linear alkyl benzens (LAB)	G	F	P	G	A	P	E
Polyalkene glycols (PAG _s)	G	G	E	G	G	P	G
Phosphate esters	V	E	P	G	A	E	F
Silicons	E	E	E	P	G	-	F
Fluorinated lubs	F	E	E	V	A	E	E

Where F = Fair, G = Good, E = Excellent, V = Varies.

In general synthetic lubricants possess the following properties.

Properties:-

- Thermal stability even at high operating temperatures.
- Chemical stability even in corrosive environments.
- High viscosity – index.
- Non – inflammability & high flash points.
- Low freezing point.

Fe typical applications of synthetic lubricants are given below:

Synthetic lubricant	Application	Remarks
Di-2 ethyl sebacate (Diester)	Used for lubrication in turbo – jets	Satisfactory performance from 50°C to 230°C
Phosphate esters	As additive in petroleum lubricants	Improves boundary lubrication properties
Poly alkene glycol (PAG _s)	Aircraft turbine lubricants	Thermally stable free from corrosive action, stable even at high rates of mechanical shear
Higher polyalkene oxides, polyglycidyl ethers	Residue free high temperatures lubricants for roller bearings of sheet glass machinery	Decompose into volatile parts at high temperatures
Fluorinated lubes	Used in submarines	Less susceptible to oxidation and cracking, high chemical & thermal stability
Silicone	Moisture – repellent dielectric lubricants for clocks, tuners & other electronic devices	Prone to oxidize at high temperatures forming gels

Mechanism of Lubrication :- Lubrication mechanism can be classified into following type:

(a) Hydrodynamic Lubrication or Fluid Film Lubrication :-

- In this, the moving / sliding surfaces are separated from each other by a bulk lubricant film (at least 1000^oA thick).
- This bulk lubricant film prevents direct surface-to-surface contact so that the small peaks & valleys do not interlock.
- This consequently reduces friction & prevents wear.
- Fluid film lubrication is shown in Fig. 2.
- The small friction is only due to the internal resistance between the particles of the lubricant moving over each other.

Figure 2.

- In such a system, friction depends on the thickness and viscosity of the lubricant & the relative velocity & area of the moving / sliding surfaces.
- The coefficient of friction $\frac{\text{force required to cause motion (F)}}{\text{Appliedload (W)}}$ is as low as 0.001 to 0.03 for fluid film lubricated system in comparison to 0.5 to 1.5 for unlubricated surfaces.

Let us now consider how the hydrodynamic film is actually generated between a bearing & a rotating journal. Fig. 3(a) shows a journal resting on the bottom of the bearing before motion.

- Fig. 3 (b) shows the oil film which separates the surfaces when the journal rotates.

Figure 3

- Light machines like sewing machines, watches clocks, delicate and scientific instruments are provided with fluid – film lubrication.
- Fluid film lubrication is satisfactorily done by hydrocarbon oils. These are generally blended with selected long chain polymers in order to maintain viscosity of the oil constant in all seasons of year.

(b) Boundary Lubrication 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.
- Solid lubricants, greases and oils with proper additives function in this manner.

A thin layer of lubricant is adsorbed on the metallic surfaces which avoids direct metal – to – metal contact. The load is carried by the layer of the adsorbed lubricant on both the metal surfaces see (Fig. 4.)

- In boundary lubrication, the distance between moving / sliding surface is very small of the order of the height of the surface asperities.

Figure 4.

- The contact between the metal surface 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 become welded together by the appreciable heat that is generated.
- This prevents motion as the two surfaces adhere together. This is known as seizure.
- If motion proceeds with the removal of some metal from one of the surface the result is known as scuffing.

For boundary lubrication the lubricant molecules should have:-

- Long hydrocarbon chains.
- Latered attraction between the chains.
- Polar groups to promote wetting or spreading over the surfaces.
- High viscosity index.
- Resistance to heat & oxidation.
- Good oiliness and.
- Low pour & oxidation.

Lubricants used for boundary lubrication are:-

- (i) Graphite and MoS_2 either as solid or stable emulsion, in oil. These materials reduce friction between metallic surfaces by forming films on the surfaces and they can bear compression as well as high temperature.
- (ii) **Mineral oils.** These are thermally stable & their adhesion property (Oiliness) is improved by adding small amount of fatty acids or fatty oils.
- (iii) **Vegetable and animal oils and their soaps** : - They possess greater oiliness compared to mineral oils.
 - They either physically adsorbed to metal surfaces or react chemically at the metal surfaces, forming a thin film of metallic soap, which acts as lubricants.

(c) Extreme Pressure Lubrications :-

It is done by incorporating extreme pressure additives in mineral oils for applications in which high temperature is attained due to the very high speed of moving / sliding surfaces under high pressure.

- In such applications, liquid lubricants fail to stick and may decompose and even vaporize
Chlorinated esters, sulphurized oils and tricresyl phosphate are examples of such additives.
- These additives react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulphide or phosphides, in the form of durable films.
- These films can withstand very high loads and high temperatures because of their high melting points.
- Hence they serve as good lubricant under extreme – pressure and extreme temperature conditions.
- These lubricants have an additional advantage that if the low shear strength films formed on the moving parts are broken by the rubbing action, they are immediately replenished.

Application which demand lubrication by extreme pressure additives :-

- Wire drawing of titanium (requires chlorine containing additive which reacts with the stable oxide film on the metal surface).

- In cutting fluids in machining of tough metals. A typical lubricant consists of hydrocarbon oil, a small amount of fatty acid as a boundary lubricant and an organic chloride or sulfide additive.
- For hypoid gears used in rear axle drive of cars which has both longitudinal sliding motion & normal rolling movements.

POLYMERS

The word “Polymer” is derived from two Greek words. Poly-many, - Units or parts Polymers = many parts or units.

- A polymer is a long molecule formed by the joining together of thousand of small molecular units by chemical bonds. Due to their large size they can be called macromolecules.
- From the molecules, which the polymer is formed is a monomer. This process is called polymerization.

Degree of Polymerization (DP):- The number of monomers involving to form a polymer in polymerization reaction is known as Degree of polymerization.

- Polymers with a high degree of polymerization are called “high polymers” and those with low degree of polymerization are called oligopolymers.
- High polymers have very high molecular weights (10^4 to 10^6) and can be called macromolecules

FUNCTIONALITY: Functionality means the no. of bonding or reactive sites in a molecule. If a molecule is having 2 reactive sites then it is called a monomer.

- When a functionality of a monomer is two (bifunctional), it will give linear straight chain polymer
For eg. Hexamethylene diamine
- When a functionality of a monomer is three (trifunctional), it will give 3 dimensional structure.

Polymer classification

According to the origin

(i) Natural (ii) Synthetic

(i) **Natural:** Polymers which are extracted from natural materials are natural Polymer.

For eg. :- Cellulose

(ii) **Synthetic:-** Polymers which are made by man are synthetic.

For eg.:- Polyethylene

According to the structure

(1) Linear (2) Branched (3) Cross-link

(1) **Linear :-** Linear in shape

(2) **Branched:-** Polymers which will be branched containing side chain.

Eg.:- Low density polyether

(3) **Cross-link :-** main chains will give rise to cross-link, 3D structure.

cross-link is always a strong polymer which will have network structure. It will not breakup easily.

Based on structure / no. of monomers:-

(1) **Homopolymer:** Homopolymer will contain single type of monomers (same type).

In this polyethylene, there are a no. of monomers of ethylene only.

(2) **Co-polymers:** Co-polymer will contain different types of (or different no. of) monomers. This process is called Co-polymerization.

These are of 4 types:-

(1) Random (2) Alternate (3) Graft (4) Block

(1) Random: A polymer contains 2 or more no. of monomers in chain by random arrangement.

A & B are two monomers

(2) Alternate: polymer containing 2 or more no. of monomers in chain by random arrangement.

A & B are two monomers

(3) Graft: polymer will contain 2 or more no. of monomers. Here homopolymer will be linked with the other homopolymer. This link or branch we will have 2nd type or other type of polymer.

This arrangement is graft arrangement.

(5) Block: Long sequence of monomers in linear.

polymerization :-It is of two types based synthesis.

(1) Addition Polymerization

(2) Condensation Addition Polymerization

Addition Polymerization	Condensation Polymerization
(1) Polymer is synthesized by addition Polymerization from same typ of monomers. Eg. Polyethetic	(1) Polymer is formed or synthesized by condensat of 2 different Eg. Nylon 6,4
(2) Elimination of small molecules will not be done	(2) Elimination of small molecules is seen like H ₂ O, CH ₃ OH, HCl etc.
(3) Polymer the exact multiple of monomer	(3) Polymer is not the exact multiple of monomer because elimination of small molecule takes place.
(4) In general, homo chain polymer gives thermoplastics.	(4) In general, hetero-chain polymer will gives thermosets.
(5) Homo chain polymer (same type monomer)	(5) Hetero chain (different monomer will be txt

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(6) In general addition, polymerization will proceed in 3 types. (1) free radical (2) Cationic (3) Anionic	(6) In condensation polymerization (1) free radical (2) Anionic (3) Cationic reactive centre are not observed.
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Plastics high molecular weight organic compounds which can be moulded by the application of heat or pressure.

These are mainly of 2 types:

- (1) Thermoplastic resins.
- (2) Thermosetting resins

(1) Thermoplastic resins: Thermoplastic resins soften on heating and become plastic so that it can be converted to any shape by moulding.

- On cooling, they become hard or rigid. On heating, they soften again & the material can be remoulded to any desired shape.

Eg. Polyvinyls, Polyethylene

(2) Thermosetting resins:- Thermoplastic resins are those which set upon heating & can't be reformed when once they are set. In general those resins, which are formed by condensation are thermosetting.

- It will give 3 dimensional structure & high molecular weight.

Eg. Bakelite, Dacron.

Thermoplastic resins.	Thermosetting resins
(1) Thermoplastics are formed by addition polymerization.	(2) Thermosetting resins are formed by condensation polymerization.
(2) Molecular weight will not change on heating.	(2) In this molecular weight will increase with the formation cross-link structure.
(3) They soften on heating readily & can be reshaped.	(3) They do not soften on heating and can not be reshaped or remoulded.
(4) They are usually soft, weak and less brittle.	(4) They are usually hard, strong and more brittle.
(5) They can be regenerated from wastes.	(5) They are regenerated from wastes.
(6) They are usually soluble in some organic solvents.	(6) Due to strong bonds & cross-links, they are insoluble in almost all organic solvents.
(7) In this van der Waals' forces are present H-bonding is also seen.	(7) In this covalent bonds are seen.

Examples for Thermoplastic resins

(1) Polyvinyl Chloride (PVC):

- Vinyl chloride will undergo polymerization to give PVC.
- PVC is obtained by heating a water – emulsion of vinyl chloride in presence of a small amount of benzyl peroxide or hydrogen peroxide in an autoclave under pressure.

PVC is of two types:

- (1) Plasticized PVC
- (2) UnPlasticized PVC or Rigid

Properties:

- PVC is colourless, odourless & non inflammable.
- PVC is resistant to light, to flame & to chemicals.
- Highly rigid, stiff but also brittle.
- It is insoluble in common solvents.

Applications:

(1) Rigid or unplasticized PVC:

- It is used for making pipes for drainage & guttering.
- It is used for making sheets, which are employed for light fittings, safety helmets, refrigerator components & tyres.
- Rigid is as it is PVC.
- Used to prepare bottles, ladies handbags.

(2) unplasticized PVC: It is obtained by adding plasticizers such as dibutyl phthalate, trioxslyphosphate dioctyl phthalate etc.

- It is used for plastic rain wear.
- It is used for baby paints.
- PVC pipes, PVL shoes, for beach wear.
- PVC, is the water proof materials.

(2) Polyethylene (PE) :- There are 2 types of polyethylene.

- Low density polyethylene (LDPE)
- High density polyethylene (HDPE)

1. Low density polyethylene (LDPE):-

Preparation: It is prepared by polymerizing ethylene at high pressure of 1000-5000 atm. & at 250^o C in the free initiator CO₂.

2. High density polyethylene (HDPE)

- Low density.
- Low crystallinity
- Chemically inert & has good chemical resistant
- Excellent electrical insulation property.
- Tough & flexible even at low temp.

Uses: LDPE is used in following application

- Films for general packaging and carrier bags.
- Squeeze bottles particularly for detergents
- Moulded toys
- Ink tubes for pens & mugs.

Liminations:

- LDPE is permeable to gaes.
- Because of low density & crystallinity
- LDPE has low rigidity & is not suitable for load bearing application

(2) High density polyethylene

Preparation: Ethylene is polymerized under 6-7 atm pressure at 60-70° C in the presence of Zeiglar – natta catalyst $[TiCl_4 + Al(C_2H_5)_3]$

Properties:

- Molecules are linear so HDPE has high density & more % crystallinity.
- Softening temp. is higher.
- Excellent chemical resistance.
- Good electrical insulation property.
- Low water & gas permeability.
- Free from odour & toxicity.
- More stiff, hard & possesses greater tensile strength.

Uses: Used as wrapping material

- Bottles of milk, household chemicals & drug packaging are also made from it.
- Used for domestic water & gas piping

(3) Polytetra fluoro ethylene (PTFE):- (Teflon)

Preparation: Teflon is prepared by the polymerisation of tetra fluoroethylene under pressure in the presence of benzoyl peroxide as catalyst

Properties: High density & low coefficient friction.

- Chemical inertness over a wide temp, range & non adhesive.
- Excellent toughness & heat resistance.

Applications: wires & cable insulation

- Coatings of frying pans.
- Laminates for printed circuitry
- Non-lubricating bearings
- Insulators for motors, generators.

(4) Nylon:-

Preparation:

- Synthetic fibre forming polyamide are termed as nylons. Nylons are of different type.

Nylon 6:6

- Nylon 6:6 is obtained by the polymerization of adipic acid with hexamethylene diamine.
- The chain length depends on the time & temp. at which the condensation proceeds.
- The number 6 & 6 refers to no. of carbons contributed by the diamine & the dicarboxylic acid respectively.

Properties: it is a linear polymer having high strength elasticity, toughness & abrasion resistance.

- Melting point is 264° C.
- Moisture resistance

Uses: In making ropes

- It is used to make elastic hoisery & carpets.
- It is also used for jackeling electric wires.
- It is used in textile industry.
- Used to prepare brushes, films & gears.

Nylon 6: It can be made either by self condensation of E-amino caproic acid or by ring opening polymerization of caprolactm.

Nylon 11: It is made by self condensation reaction of co-amino.

Nylon 6,10: It is made by the condensation reaction of hexamethylene diamine & dibasic acid.

Application of Nylon:

- Nylon 11 is used for making flexible tubing.
- Nylon 6,6 is used in mechanical engineering.

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- Nylon 6,10 is suitable for monofilament which are used for bristles, brushes etc.
- Nylon 6 is used for making tyre cords.

(5) Bakelite :(Thermosetting resin)

Phenolic resin

- This is formed by condensation product of phenol & formaldehyde. These are known as phenol formaldehyde resins (PF resins)

- Phenol, formaldehyde may not be in same proportions in this phenolic resins.
- Phenol, formaldehyde ratio can more than one or less than one.
- If phenol, formaldehyde is more than 1 then phenol will be in excess.
- Phenol formaldehyde ratio will effect the product.

If phenol formaldehyde ratio is greater than 1 it will result in Novolac formation in the presence of acid.

- This is linear low polymer called Novolac.
- If phenol formaldehyde is less than 1 in alkaline media will result into linear called Resole.

- Here formaldehyde will be in excess.
- This Novolac Resole under some process fuse to form Bakelite independently.
- Bakelite is a thermosetting of resin which is a cross link (net) structure--> which is a very hard polymer.

Properties

- It is resistant to electricity, moisture & chemical.
- It is very hard, rigid & strong materials.
- It is scratch resistor.
- They are usually dark coloured (pinkish brown)
- Low molecular weight grades have good bonding strength
- Good adhesive

Uses:- These are used in electric field, in automotives, radio T.V. parts.

- Production of ion exchange resins.
- Electric insulator production.
- Decorative & varnishes preparation.

RUBBER:- It is one of naturally occurring polymer which has elastic properties in excess of 300%.

- That is why rubber band can be stretched to nearly 4 times of their original strength.

Rubber is of two types-

- (1) Natural (2) Synthetic

Natural rubber: The main source of Natural rubber is the sap of tree called weaver's tree (*Hevea brasiliensis*) and the latex of *Parthenium* is another important source of Natural rubber. This is seen mainly in countries like India, Malaysia, Indonesia, Ceylon etc.

- It consists of basic material latex, which is a dispersion.

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- Natural rubber is a cis-configuration. Due to this cis-configuration about the double bonds, the chains do not fit together well.
- Hence there are only weak Vander waal's forces

Schematic representation of coiled elastomers chain of natural rubber (poly isoprene)

Isolation or extraction from latex:-

- To extract rubber from latex at first a groove is cut around the tree & collect latex in a pot.
- Latex is a milky suspension containing 2-40% rubber, while the remainder is made up of mainly water & small quantities of protein & resinous material.
- When we cut the bark(tree), it will give some gummy liquid called latex. This process is called tapping. This can be done once in every six months.
- Latex contains 60% water, 35% hydrocarbons, proteins, enzymes & organic acid, 3% fatty acids, 0.5% inorganic salts & 1% esters.
- To obtain rubber from latex following steps are used.

(1) Sieving (2) Dilution (3) Coagulation

(1) Sieving:- It is the first step, in this step latex is pass through a sieve, due to the bigger impurities like leaves, bark, dirt etc., can be easily be removed.

(2) Dilution:- latex is diluted to about 15-20% rubber then strained again.

(3) Coagulation:-For this, a small amount of NH_3 is added as a preservative to the latex, then it is co-agulated by the addition of 5% solution of acetic acid or formic acid of 90% strength. The co-agulated is washed & dried.

Gutta percha & Balata rubber

- This is obtained from the mature leaves of the trees known as *Dichopsis gutta* & *Palaguim gutta*. These leaves are treated with water at 70°C for ½ an hour & then dropped into cold water. Then this Gutta percha rubber will float on the water & can be collected.
- It is very tough, it burns at 100°C.
- Gutta percha rubber is a trans form of rubber.

Trans- polymer of isoprene
(Gutta – percha rubber)

Cis rubber	Trans rubber
➤ Obtained from <i>Hevea brasiliensis</i>	➤ Obtained from Gutta tree
➤ It is prepared from cutting the tree	➤ It is prepared from mature leaves of plants
➤ Mostly formed in North America	➤ Mostly formed in Sumatra & Malaya
➤ It is cis form of isoprene	➤ It is the trans form of isoprene

Elastomers: An elastomer is vulcanizable man made rubber like polymer, which can be stretched to at least twice its length, but it returns to its original shape.

Synthetic rubber:

1. styrene rubber or Buna – S or (GR-S) (styrene buta rubber)
2. nitrile rubber (GR-A) (Buna – N)
3. neoprene or polychloroprene or (GR-M)

1. **styrene rubber or Buna – S or (GR-S) (styrene buta rubber):**- Buna – S is a co-polymer of about 75% butadiene & 25% styrene. The two components above are allowed to react in a mixing vessel containing an emulsifying

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agent. Initiators like H_2O_2 were used in the presence of anti-freeze, to produce cold SBR or "Cold rubber"

Properties:

Buna-s resembles natural rubber.

- it gets oxidized readily in oils & solvents.
- It can be vulcanized same as natural rubber; but it requires less amount of sulphur.

Uses:-

Useful for lighter dirty tyres, molded goods.

- Unvulcanized sheet, rubber, flooring & for electrical insulations

2. (Buna -N) Nitrile rubber (GR-A), General rubber Acrylonitrile:

- It is co-polymer of butadiene & acrylonitrile.
- The technique of emulsion polymerization is used for the synthesis.

Properties:

- These rubber have swelling, low solubility, good tensile strength & abrasion even after immersion in gasoline or oils.
- Rubbers have good heat resistance.

Uses:-

- Used as adhesives for fuel tanks gasoline hoses.
- They are used to make printing rollers, oil resistant & automobile parts.

3. Butyl rubber (GR-I):- It is a co-polymer having 98% isobutylene & nearly 2% butadiene

Catalyst: AlCl_3 anhydrous + CH_3Cl

Properties: Low permeability to air & other gases.

- Under normal conditions butyl rubber is amorphous.
- Resistant to heat, chemicals & polar solvents & also to ozone layer.

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- Good electrical insulator.

Uses: It is used as inner tubes.

- Used in the preparation of automobile parts, belts & tyres.
- Cable insulator

(4) Neoprene: It is a co-polymer of chloroprene.

- Chloroprene is obtained by dimerisation of acetylene to vinyl acetylene followed by HCl.

Properties: It possess high tensile strength

- Resistant to petroleum oils & gasoline

Uses: Linings of oil tanks

- Wire insulations & gaskets are prepared.

Vulcanization: To improve the properties of rubber Charles Good year (1839) discovered a process called vulcanization.

- This is the process where some compound especially "sulphur" is heated along with rubber, it will be added to the rubber the product will become more & more stiff
- When Charles scientist heated sulphur along with rubber, the tensile strength, elasticity & resistance to swelling are increased very much. This introduction of sulphur to the natural rubber is called vulcanization.
- In vulcanization sulphur is introduced to make the rubber more stiff at 110° - 140°C.
- Linear polymer (natural rubber) will result in cross - link polymer which is very rigid (vulcanized rubber)
- This stiffness depends on the sulphur quantity.
- Tyre rubber contains 3-5% sulphur.
- Battery case contains 30% sulphur.

Vulcanization can be carried out in several ways-

- (i) The article is immersed in hot water under pressure.
- (ii) The article to be Vulcanized are heated with steam under in fire house.
- (iii) By heating in fire house.

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(iv) By heating in air or CO₂.

- Ordinary soft vulcanized rubber is 1-5% sulphur, hard rubber 40-46% of sulphur

Properties: It has good tensile strength & can bear a load of 2000 kg/cm² before it breaks.

- Water resistance is improved.
- Has higher resistance to oxidation & to abrasion.
- It is very easy to shape.
- It has useful working temperature range -40^o C to 100^o C

Uses:- Manufacture of tyres, gaskets.

- Rubber threads are used to shock absorber cords heat bands for spectacles , helmets, golf balls etc.

Smoked rubber: when latex is mixed with acetic acid in along tank. It should be kept constant for 15-16 hrs.

- The product is passed through rollers by continuous water spray.
- These sheets are subjected to smoke treatment for 4 days at 60^o C
- The coloured rubber is obtained called smoked rubber.