Unit-4, Glass

Introduction :-

Glass is an inorganic substance, hard, brittle, amorphous mixture of silicates of calcium, sodium or other metal. It has no definite composition.

Ingredients — Silica, soda ash and lime stone along with borax, potash, zinc oxide, barium carbonate etc.

Glass may be considered as super cooled liquid of infinitely high viscosity.

Soda lime glass is used for water glass,
Lead glass is used for decorative cut glassware,
Borosilicate glass is used for making ovenware, and laboratary glassware.

Composition of glass :-

Chemically glass is a mixture of metallic silicates. It can be represented as

$$x R_2O . y MO . 6 SiO_2$$

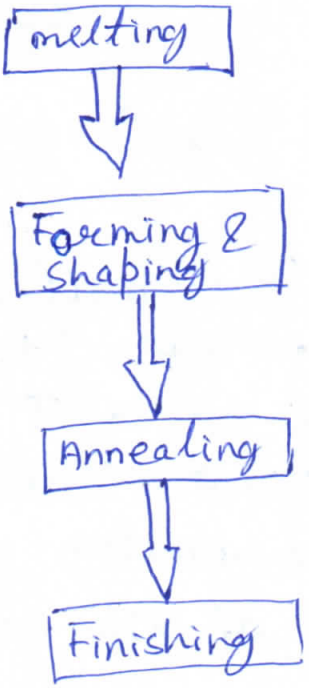
R = alkali metals (Na, K etc)
M = Bivalent metals (Ca, Pb, Zn)
x & y = whole numbers

Raw material used for different purpose of glass

S.N.	material	Purpose
1)	Na_2CO_3 (Soda ash)	Source of Na_2O to prepare soft glass known as Soda glass (water glass)
2.	$CaCO_3$	Source of CaO, CaO makes glass resistant to water, weathering and chemicals
3	Sand (SiO_2)	Imparts strength and resistant to water
4	Litharge of red lead (PbO)	Increase the refractive index and electrical resistance of glass.
5.	Borax ($Na_2B_4O_7 \cdot 10H_2O$)	Souce of B_2O_3, used as fluxing agent It decreases the expension coefficient.
6.	Zinc oxide	↓es the effect of sudden change in temp. and expansion coefficient. Gives brightness
7.	Potash Feldspar $K_2O \cdot Al_2O_3 \cdot 6H_2O$	souce of K_2O, imparts hardness and superior quality of glass
8.	P_2O_5	provides brighness for table wares.
9.	Refining agent	like Na_2SO_4, $NaNO_3$, NaCl etc. for removal of bubbles.
10.	Colouring agent	
	FeO & Cr_2O_3	green colour
	CoO	Blue
	CuO	Red
	Fe_2O_3	Brown
	SeO	Red
	Cu^{2+} salt	Peacock Blue
	$Ca_3(PO_4)_2$	milky white
11	Cullent (glass pieces)	Broken glass pieces makes melting easy

manufacturing of glass

steps of manufacturing



1) **melting** :- Finally powdered raw material mixed with cullet (broken glass prices) is fused in pot furnace or in tank furnace.

Pot Furnace	Tank Furnace
1) Used for making special glasses like optical or fine glasses	used for large scale production like bottle and water glasses
2) The constituent mixture is stirred and uniformity is achieved	Stirring is not possible so uniformity is not achieved.
3) As pots are closed and special type of glass is prepared	It is not protected & ordinary and bulk production is achieved
4) Process is stepwise	Process is continuous

Chemical reactn involved during manufacturing

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2\uparrow$$

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \rightarrow \underset{\text{glass}}{Na_2O.CaO.6SiO_2} + 2CO_2\uparrow$$

Raw material (batch) is melted in pot / tank, which are lined with firebricks. A certain amount of broken glass known as cullet is also added to decrease melting point. The mixture is heated about 1500°C by the combustion of produes gas. CO_2 escapes out of the molten mass. MnO_2 is added to decolouring. The heating process continues till the molten mass is free from glass balls & bubbles. After that it is cooled at 800°C

(2) Forming and shaping (moulding) :-

The glass articles are shaped manually or by machine, into articles of desired shape by pressing between rollers.

(3) Annealing :-

To reduce strains, it is necessary to cool down glass slowly which is known as annealing. It involves two steps

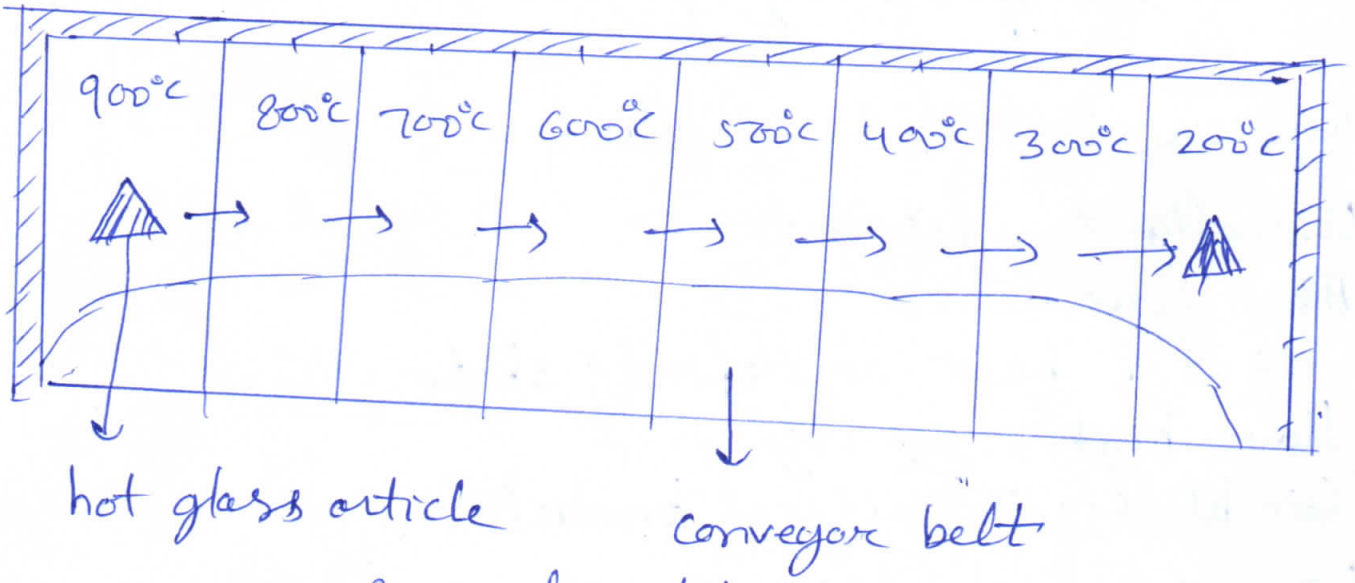
(a) Holding a mass of glass above a certain

critical temperature, long enough to reduce internal strain by plastic flow.

(b) cooling the mass to room temperature.

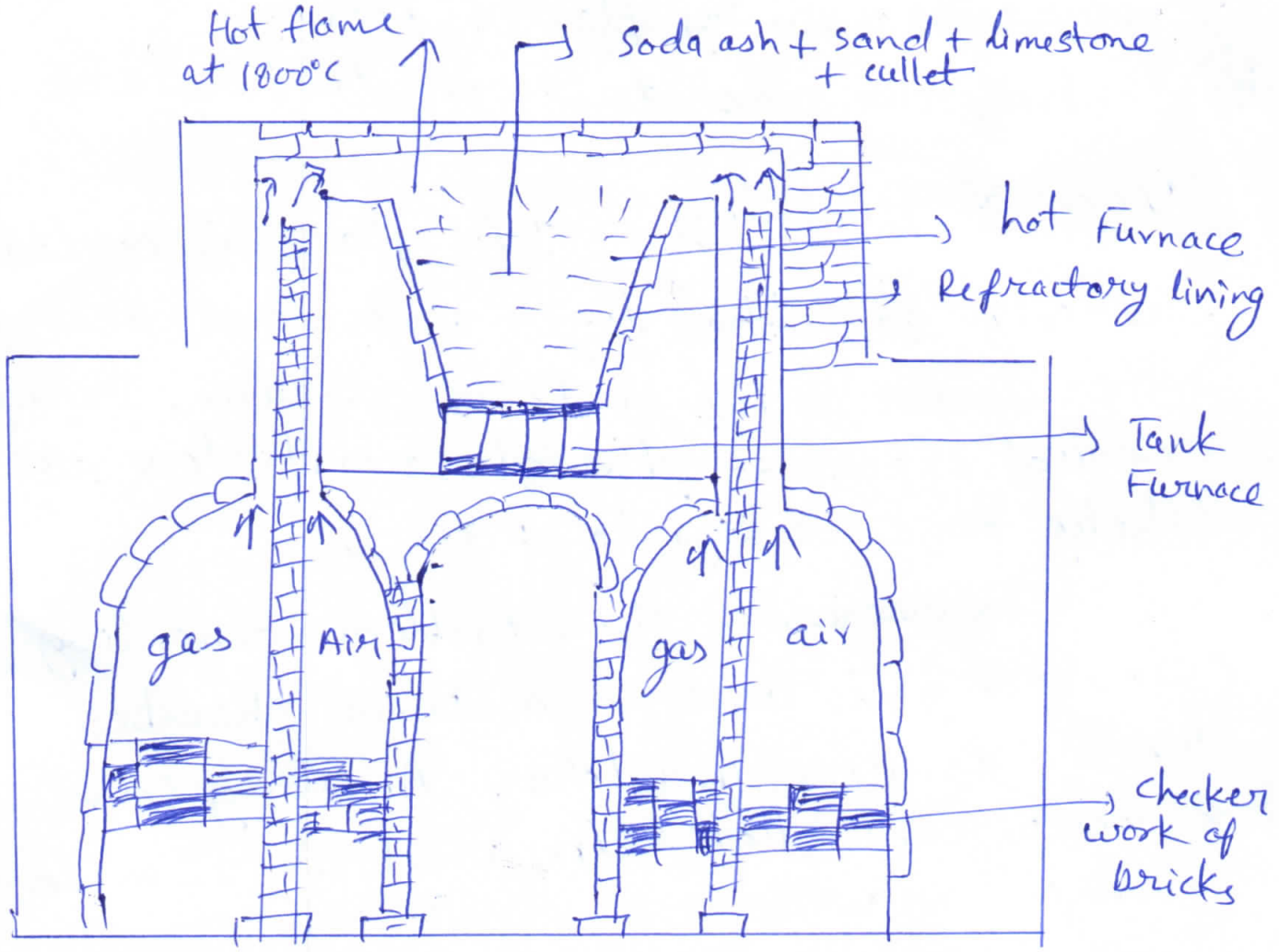
Need of Annealing :- If glass is cooled suddenly, its upper layer cools down leaving inner layer in the state of strain. During unequal expansion, the glass articles are likely to crack into pieces.

To overcome this problem, annealing (slow cooling) is done in a special chamber known as Annealing Lehr. Annealing lehr is a temp. controlled kiln which is 25 m long and 1-3 m wide.



Annealing Lehr

(4) Finishing :- It includes, cutting, polishing, grinding, exterior colouring, cleaning, metallic lining etc. for improving surface finish



Manufacturing of glass by Tank Furnace

Physical Properties of glass

1) Usually transparent
2) Amorphous solid
3) Hard & have no definite shape
4) Have high viscosity
(5) Completely vitrified product

Chemical Properties

1) Not attacked by air, water or oxidising agent
2) Alkaline in nature
3) Readily attacked by alkali
4) Resistant to acid except HF

$$Na_2O.SiO_2 + 6HF \rightarrow 2NaF + SiF_4 + 3H_2O$$

$$CaO.SiO_2 + 6HF \rightarrow CaF_2 + SiF_4 + 3H_2O$$

Types of glasses

1) Soft glass (Lime-soda-silica glass)

It is made by fusing Na_2CO_3, $CaCO_3$ & SiO_2. Its approximate composition is $Na_2O.CaO.6SiO_2$

Properties

(a) low cost
(b) Resistant to cement & water
(c) lower melting point
(d) Attacked by common reagents like acids

(2) Uses - window glasses, Tablewares like bottles, jar etc., glasswares in lab.

2) Hard glass (Potash lime)

It is made by fusing SiO_2, $CaCO_3$, K_2CO_3 and its average composition is - $K_2O.CaO.6SiO_2$

Properties

(a) more costly
(b) High m.p.
(c) more resistant to acid and alkali
(d) Fuse with difficulty

Uses - chemical Apparatus, combustion tubes

3) Borosilicate glass / pyrex glass or Jena glass

These are hard and presence of boron oxide reduces co-efficient of thermal expansion and

these are very resistant to thermal shock and not attacked by chemicals. It is prepared by fusing sand, borax and aluminium oxide along with Na_2O and K_2O.

Uses - It is resistant to action of water and other chemical, also withstand upto a high temp. so used for making lab. wares, chemical plants & television tubes.

4) Glass wool :-

Fibrous wool like material composed of intermingled fine filament of glass. These are made by action of steam jet on creeping molten glass down from very fine holes.

Properties -

(a) Non combustible and fire proof
(b) Poor conductor of electricity
(c) Heat proof
(d) Resistance to most chemicals
(e) Very high tensile strength

Uses -

Electrical & sound insulation, heat insulation in domestic and industrial appliances, For filteration of corrosive liquids like acids. In manufacture of glass fibre.

(5) Safty glass :- These are of two types

(a.) A single glass sheet is preheated and air is blown over its surface. Rapid surface cooling produces a hard contracted film which keeps the entire sheet in compression.

(b) It is prepared by placing a thin layer of plastic (either acetal resin / cellulose acetate) between two sheets of ordinary glass. This is then heated under high pressure till the glass layers and plastic layers are bonded into one another.

Properties – Shatter proof, shock proof

Application / uses

Windshield in automobiles and aeroplanes

Bullet proof glass, Laminated glass.

Unit-4-Cement

Cement is a finely grey coloured mineral powder which has cohesive & adhesive properties. The material is capable of binding materials like sand, stone, bricks etc.

Classification of cement :-

(1) Natural cement :- Manufactured by calcining a naturally occuring argillaceous lime stone

(2) Pozzolana cement :- Volcanic ash mixed with lime & heated

(3) Slag cement :- Furnace slag + hydrated lime

(4) Portland cement :- Calcining at about 1500°C an intimate mixture of clay & lime.

Chemical composition of Raw material

	constituent	% range by mass	Function
1	Lime (CaO)	60 – 70	↑ strength
2	Silica (SiO_2)	17 – 25	↑ strength & Prolong setting time
3	Alumina (Al_2O_3)	3 – 8	↑ strength but reduces setting time
4	Iron-oxide (Fe_2O_3)	2 – 4	Impart grey colour ↑ strength & hardness
5	MgO	1 – 5	contribute to soundness
6	SO_3 (sulphur tri oxide)	1 – 3	Imparts soundness if present in small amt.
7	Alkali-oxide Na_2O / K_2O	0.3 – 1.5	causes efflorescent

Manufacturing of Port land cement by Rotary kiln :-

Raw materials

(1) Calcareous material — supplies lime CaO
(2) Argillaceous " — supplies Silica, Fe_2O_3, Al_2O_3
(3) Fuel oil / Powder coal :- supplies heat
(4) Gypsum :- Help to prolong setting time or retard setting action.

These are two types of Process

Dry Process	Wet process
1) Slow	Fast
2) Inferior quality of cement	superior quality
3) Adopted when raw material is hard & Dry	Adopted when raw materid is soft.
4) cheaper	costly

The complete manufacturing involves the following steps :-

(1) Crushing of raw material
(2) Mixing
(3) Burning
(4) Grinding
(5) Packing

The most important part of manufacturing of cement takes place in Burning step. - After mixing, raw material is fed into the Rotary Kiln, where actual chemical changes occur.

Rotary Kiln is a steel tube about 2.5-3.0 m in diameter & 90 to 120 m in length, lined inside with refractory bricks. It is slightly inclined downwards towards the exit and can be rotated at desired speed. It has three zones

(i) Upper Zone / Dry Zone :-

Temp-range is 100 - 400°C & most of the moisture is removed here.

(ii) Calcination zone (central Part)

The temp. is about 1000°C Here limestone undergoes decomposition to form quick lime and CO_2

$$\underset{\text{Limestone}}{CaCO_3} \longrightarrow \underset{\text{quick lime}}{CaO} + CO_2\uparrow$$

(iii) Lower part (Burning Zone)

Temp. range is 1500 - 1700°C

The mixture melts and form little rounded hasty masses about the size of pea, which

are known as clinkers.

The reactions taking place:-

$2\,CaO + SiO_2 \rightarrow Ca_2SiO_4$

dicalcium silicate (C_2S)

$3\,CaO + SiO_2 \rightarrow Ca_3SiO_5$

Tricalcium Silicate (C_3S)

$3\,CaO + Al_2O_3 \rightarrow Ca_3Al_2O_6$

Tricalcium aluminate (C_3A)

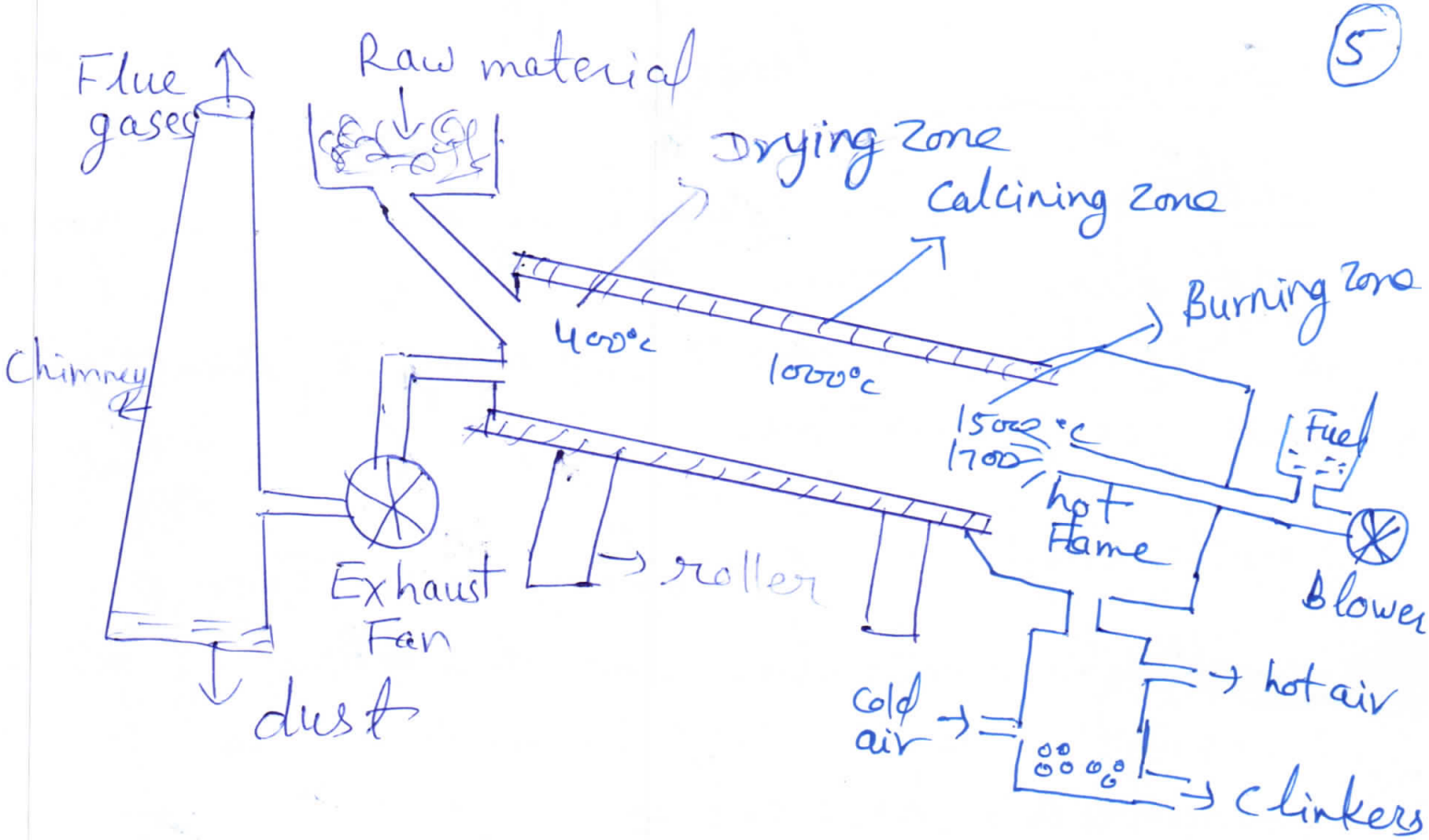
$4\,CaO + Al_2O_3 + Fe_2O_3 \rightarrow Ca_4Al_2Fe_2O_{10}$

Tetra calcium alumino Ferrate (C_4AF)

Grinding —

After cooling, the clinkers are converted into fine powder in grinding mills. 2-3% of Gypsum is mixed with clinkers during grinding which retard setting process.

Packing:- The ground cement is stored in silos and packed into bags.



Rotary Kiln for cement manufacture

composition of constitutional compounds of cement :-

compound	Formula	Av. %	setting time
Tricalcium silicate	$3CaO.SiO_2$	45	7 days
Dicalcium Silicate	$2CaO.SiO_2$	25	24 days
Tetra Calcium alumino Ferrate	$4CaO.Al_2O_3.Fe_2O_3$	9	1 day
Calcium Sulphate	$CaSO_4$	5	—
Tricalcium aluminate	$3CaO.Al_2O_3$	1	1 day
Calcium & Magnesium oxide	CaO	2	—
	MgO	4	—

Setting & Hardening :-

Setting :- When cement is mixed with water and allow to stand, it sets into a hard & rigid mass due to chemical reaction and gel formation.

Hardening :- Converting into compact rock like material and developing of strength due to crystallisation is known as hardening.

The process of setting & hardening of cement are believed to be partly a chemical & partly a physical changes.

Chemical change – Hydrolysis
Phy. " – Gel formation

Hydrolysis :-

$$3\,CaO.SiO_2 + 3\,H_2O \rightarrow 3\,CaO.2SiO_2 + Ca(OH)_2$$
(aq)

or

$$3\,C_3S + 3\,H_2O \rightarrow C_3S.3\,H_2O + Ca(OH)_2$$
gel

Hydration :-

$$3\,CaO.Al_2O_3 + 6\,H_2O \rightarrow 3\,CaO.Al_2O_3.6\,H_2O$$
crystal

Hardening takes place due to interlocking of these crystalline products formed during hydration.

Mostly setting takes 24 hours whereas hardening requires 15-20 days

Chemical reactions taking place during setting & hardening :-

(1) When cement is mixed with water, the paste so formed becomes stiff within a short time. This intial set or Flash set is due to the presence of Tricalcium-aluminate (C_3A) which hydrates very rapidly

$$3CaO.Al_2O_3 + 6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O + \text{heat}$$

or

$$C_3A + 6H_2O \rightarrow C_3A.6H_2O + \text{heat}$$

crystals

Flash set is not desirable because it prevents hydration of cement constituents.

So Gypsum is added to retard Flash setting.

(2) Gypsum reacts with C_3A to form insoluble complex, which does not hydrates rapidly

$$3CaO.Al_2O_3 + xH_2O + y\,CaSO_4.2H_2O \rightarrow$$

$$3CaO.Al_2O_3.y\,CaSO_4.2H_2O$$

insoluble complex

or

$$C_3A + xH_2O + y\,CaSO_4{\cdot}2H_2O \rightarrow C_3A.\,y\,CaSO_4{\cdot}z\,H_2O$$

(3) Tetra-alumino Ferrate undergo hydrolysis to form crystalline compound & gel.

$$4\,CaO.Al_2O_3.Fe_2O_3 + 7H_2O \rightarrow 3\,CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3.H_2O$$

(Crystal; gel)

or

~~4~~ ~~Ca_4Al~~

$$Ca_4AF + 7H_2O \rightarrow C_3A.6H_2O + CF.H_2O$$

(Crystal; gel)

(4) Tricalcium silicate hydrates within 24 hr and hydration completes in 7 days

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

(Tobermonite gel)

or

$$2\,C_3S + 6H_2O \rightarrow 3\,C_3S.3H_2O + 3\,Ca(OH)_2$$

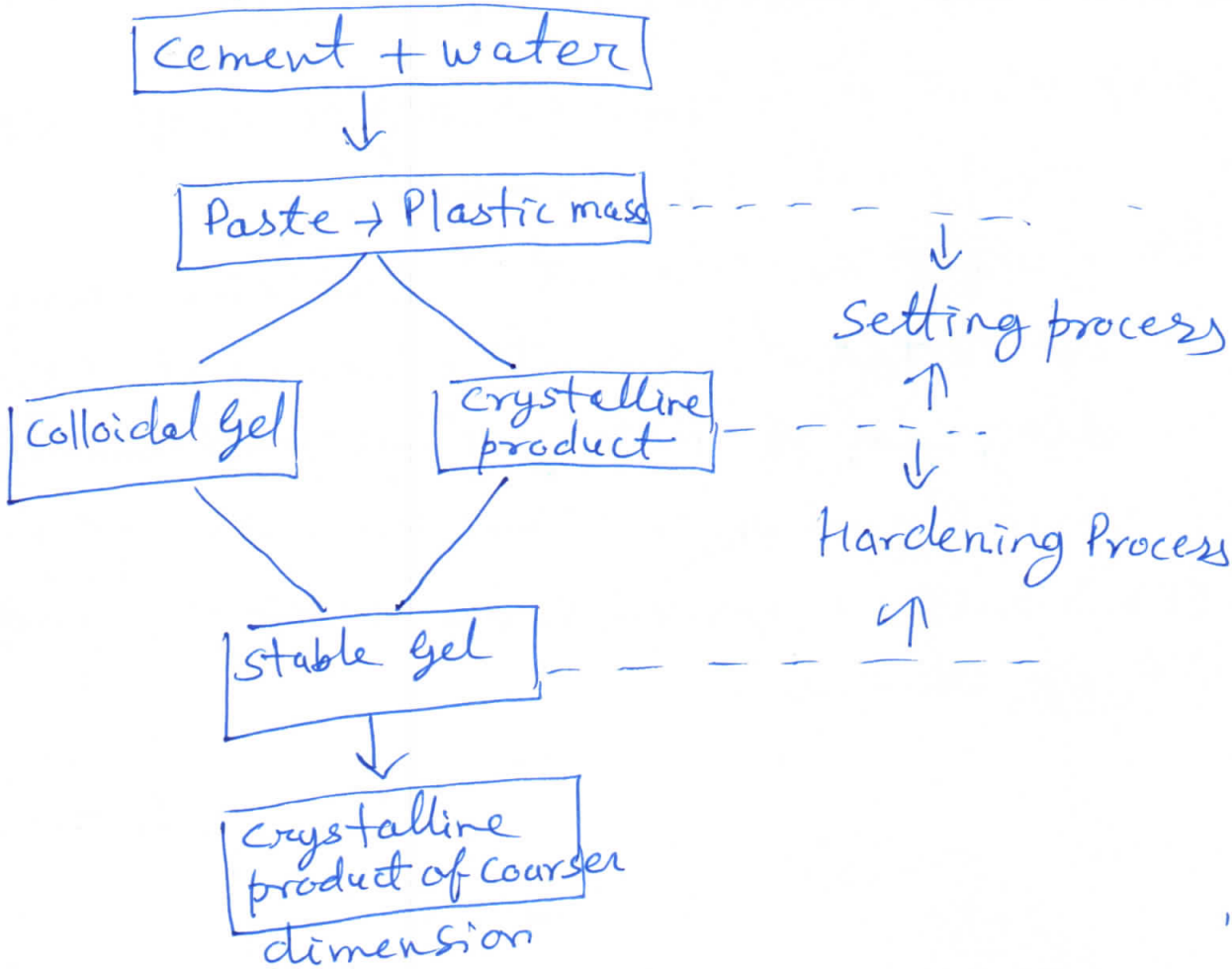
Tobermonite gel serves as bonding material between grains of sand, stone, bricks etc. The strength of cement in early days is due to formation of this gel.

(5) Dicalcium silicate also forms Tobermonite gel when reacts with water but slower (7 days to 28 days)

$$2(2CaO.SiO_2) + 4H_2O \rightarrow 3\,CaO.SiO_2.3H_2O + Ca(OH)_2 + \text{heat}$$

(Tobermonite gel)

(6) These gel & crystal products harden gradually to form hardened mass. As the hydration & hydrolysis process goes on, the set mass gains strength within 10 to 28 days.



Role of Gypsum :- It is added during the grinding of clinkers. It retards the setting process or Prolongs setting time.

Gypsum is $CaSO_4 \cdot 2H_2O$

$$CaSO_4 \cdot 2H_2O \xrightarrow{110-130^\circ C} CaSO_4 \cdot \tfrac{1}{2} H_2O + 1\tfrac{1}{2} H_2O$$

Cal. Sulphate hemi hydrate (POP)

$$CaSO_4 \cdot \tfrac{1}{2} H_2O \xrightarrow{175-205^\circ C} CaSO_4 + \tfrac{1}{2} H_2O$$

anhydrate

Assignment – 4

10

(1) What is Flash setting?

(2) What is the role of Gypsum in cement manufacturing?

(3) What is the chemical composition of raw materials of cement.

(4) What is the composition of constitutional compounds of cement

(5) What is cement? Explain manufacturing of Portland cement with neat & clean diagram of Rotary Kiln process. Also give chemical reactions involved.

(6) Write a short note on setting & hardening of cement.

At every 1°C rise of temp., test flame is introduced for a moment, by moving the shutter. The temp. at which a distinct flash seen inside the cup, is noted as flash point. (11)

When the oil ignites and continuous to burn at least for 5 second the temp. is noted as the fire point of the oil.

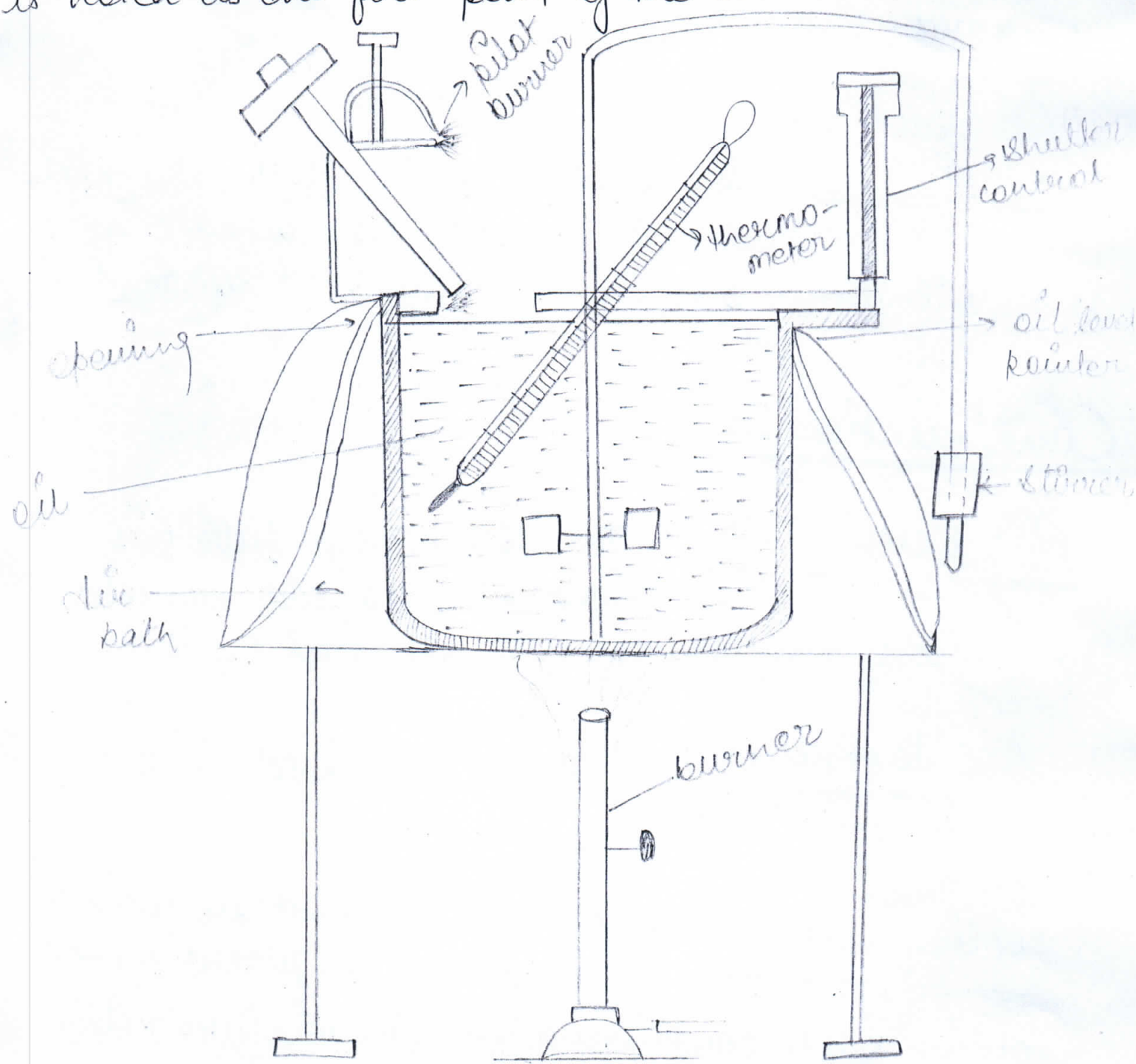


Fig:- Pensky-Marten's Flash point Apparatus

Cloud and pour point :-

Cloud point :- Cloud point is the temp. at which oil becomes cloudy or hazy in apparatus. when it is cooled in a standard apparatus at a standard rate.

Pour Point :- pour point is the temp. at which oil just ceases to flow when cooled at a standard rate in a standard apparatus.

Construction :-

1. **Flat Bottom Tube :-** The flat bottom tube has height of 12 cm and diameter of 3cm the thermometer is mounted on it.

2. **Air Jacket :-** The tube is enclosed in a air jacket.

3. **Cooling Bath :-** The jacket is enclosed in turn by a thermometer is placed inside cooling bath containing freezing mixture (Ice + Nacl). A

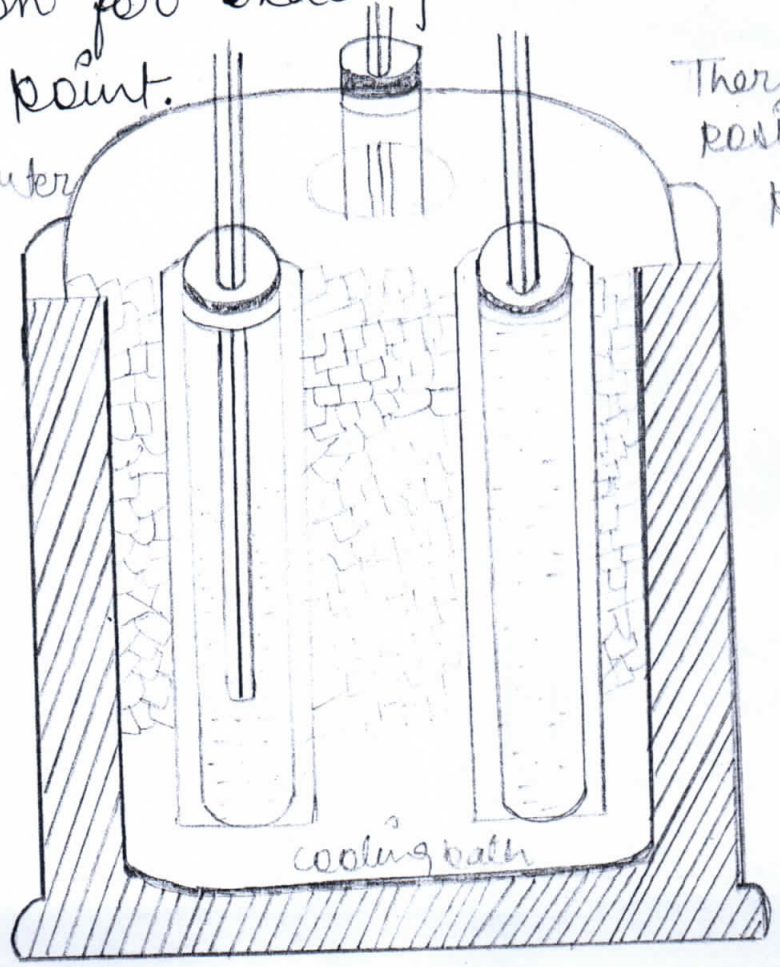
Working :- Lubricating oil to be tested is filled inside the tube. The thermometer is placed inside the oil and in cooling bath and the cork is fitted to the mouth of the tube.

The tube is placed in the cooling air jacket enclosed by the cooling bath containing the cooling mixture.

The temp. of air will start reducing down.

At every 1°c fall in temp. of oil, the tube is out from the jacket and observed for the cloudiness.

The test is continued until no movement of oil is noticed, when the test jar is held in a horizontal position for exactly 5 seconds. This temp. is the pour point.

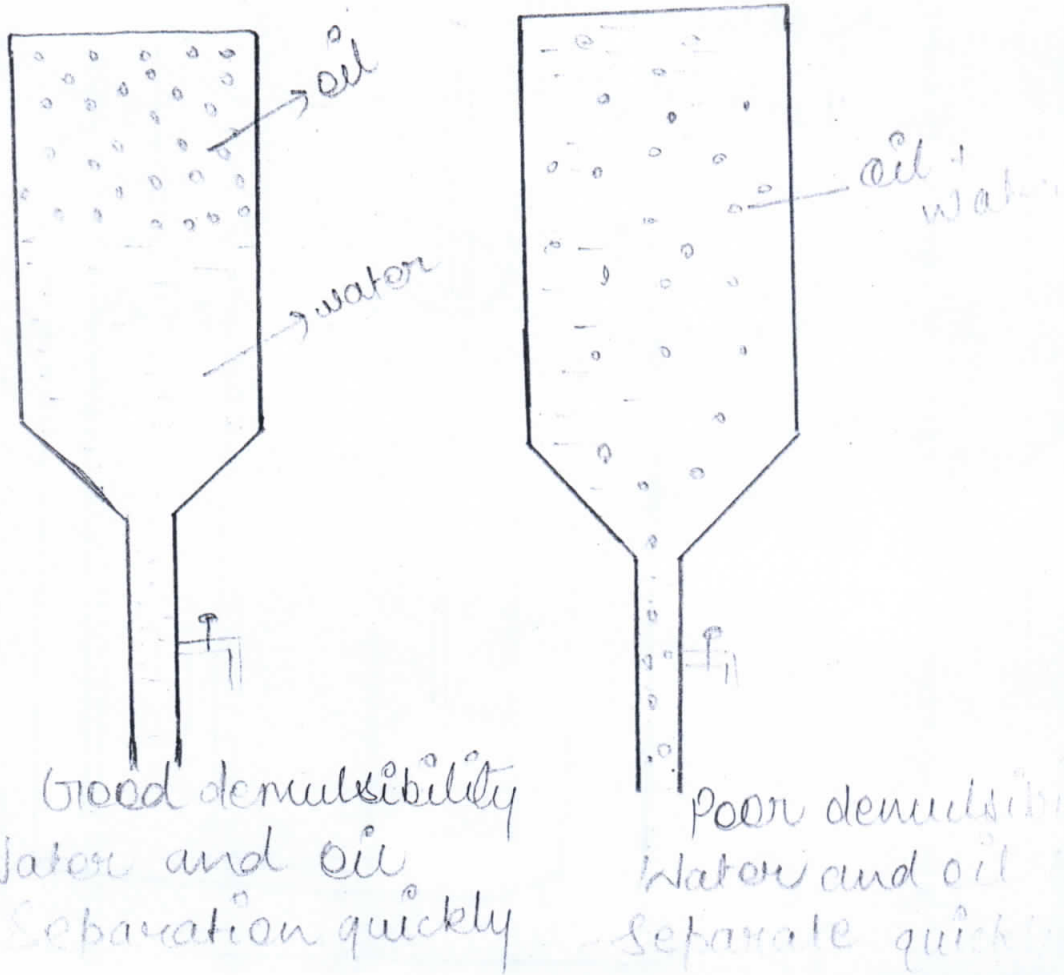


Emulsification :-

Emulification can be defined as the ability of the oil to get intimately mixed with water. it can be oil in water emulsion or water in oil emulsion. Emulsion has a tendency to collect dirt, grit particles and other foreign matters, thereby causing an abrasion and wearing out of the machinery.

Significance :-

1. the higher the emulsification number, better is the oil for application. In cutting operation, emulsion act as a coolant as well as a lubricant.



UNIT- 4

LUBRICANTS

Introduction :-

A lubricant is defined as a substance which reduces the frictions when introduced between two surfaces and the phenomenons known as lubrication.

Functions of Lubricants :-

1. Acts as a coolant
2. Provides protection against corrosion
3. Reduce the surface deformation, wear and tear
4. Lubricant reduce the frictional resistance.
5. Improves efficiency of machine.
6. Acts as a seal

Classification of Lubricants :-

Classification of Lubricant on the basis of Physical State

- Lubricating oil or (liquid Lubricants)
  - 1. Animals and vegetable oil
  - 2. Mineral or petroleum oil
  - 3. Blended oil
  - 4. Synthetic lubricating oil
- Grease (semi-solid Lubricant)
  - (a) Soap grease
  - (b) Hydrocarbon
  - (c) Inorganic
  - (d) Polymeric grease
    - 1. Antifriction grease
    - 2. Friction grease
    - 3. Protective grease
    - 4. Dispersion grease
- Solid Lubricant
  - Graphite
  - MoS_2

Types of Lubrication (Mechanism of Lubrication) :-

On the basis of lubricant characteristics lubrication are of following types :-

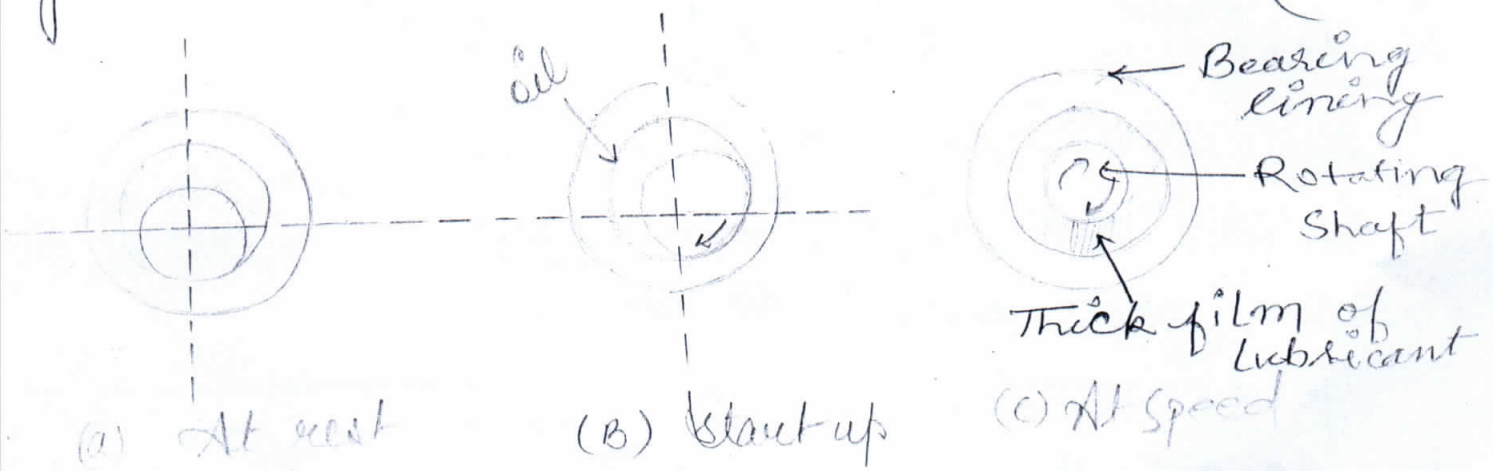
1. Hydrodynamic or fluid film Lubrication
2. Thin film or Boundary Lubrication
3. Extreme pressure lubrication

1. Hydrodynamic Or Fluid film Lubrication

A thick film or fluid (>1000 A° thick) separates the two sliding metal surfaces. the film of lubricant is absorb on the metal surface and held by vander waals force.

The bulk lubricant film prevents direct surface to surface contact so that the small peaks and valleys do not interlock. the results in reduction of friction and prevents wear and tear.

The hydrodynamic film is actually generated between a bearing and a rotating journal (shaft)



In test position, the saft rests on the bottom of bearing and thus the lubricant is squeezed out, which results in contact between shaft and bearing surfall.

When a torque is applied to the saft, it begings to rotate and shaft has tendency to roll up the bearing surface in opposite direction After start up, however, the coefficient falls rapidly.

2. Boundary Lubrication Or Thin film Lubrication :-

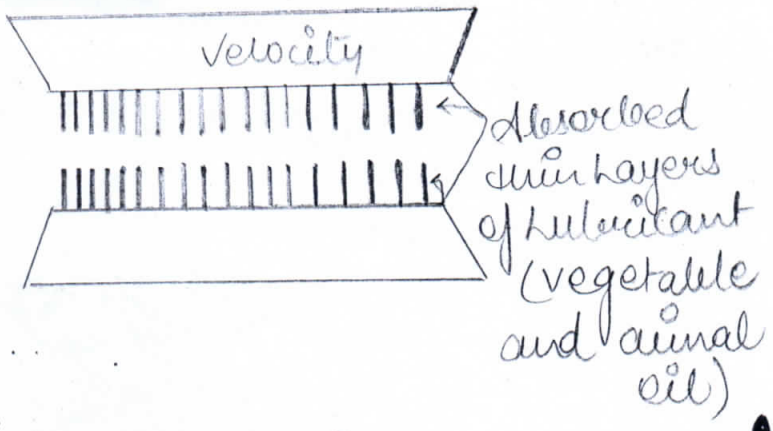
The lubrication is suitable, when a continuous film of lubricant cannot persist and direct metal to metal contact is possible because of various reasons. For example, when a shaft starts moving from test rest or speed is very low or load is very high or viscosity of oil is extremely low.

For boundary lubrication, the lubricant molecules should incorporate :-

1. Resistance to heat and oxidation
2. High viscosity index
3. Lateral attraction between chains
4. Low power and oxidation
5. Good oiliness
6. Low hydrogen

Lubricants used for boundary lubrication are:-

1. Graphite and MoS_2 either as solid or as stable emulsion in oil.
2. Mineral oils
3. Vegetable and animal oil and their soaps.



3. Extreme Pressure Lubrication:-

When the machine runs under the conditions of high load, the temp. rises between the moving surfaces of the metals. Thus, under such severe conditions ordinary fluid film i.e boundary fluid film is not effective, because it may vapourize or fail to stick on the metal surfaces.

Properties of Lubricants :-

1. Viscosity
2. Ash content
3. Acid value
4. Carbon residue
5. Oiliness
6. Volatility
7. Saponification
8. Flash and fire point
9. Aniline point
10. Cloud and pour point

Viscosity :-

Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flowability of a lubricating oil, the lower the viscosity greater the flowability. It is mainly due to the forces of cohesion between the molecules of lubricating oil.

Cohesive

$$F = \eta \frac{v}{d}$$

where η = coefficient of viscosity

if v = 1cm per second

d = 1cm

F = 1dyne

then $\eta = 1$

the unit of viscosity is poise.

Viscosity Index :-

$$\text{Viscosity Index (V.I.)} = \frac{L-U}{L-H} \times 100$$

where V.I = viscosity index

L = viscosity at 100°F of the ~~test~~ low viscosity standard oil having a V.I. of 0 (i.e. Gulf oil) and also same viscosity as the oil under test at 210°F

U = viscosity at 100°F of the oil under test.

H = viscosity at 100°F of the high viscosity standard oil having a V.I. of 100 and having the same viscosity as the oil under test at 210°F

The lubricating oil becomes thinner as the temp. rises. the rate a which the viscosity of oil changes with temp. is measured by an arbitary scale, called Viscosity Index.

Determination of viscosity by Redwood viscosity meter :-

Redwood viscometer are of two types :-

1. Redwood viscosity No. - 1 universal
2. Redwood viscosity No. - 2 Admirally

Redwood viscosmeter No.-1. :-

construction :- Redwood viscometer consist of following parts :-

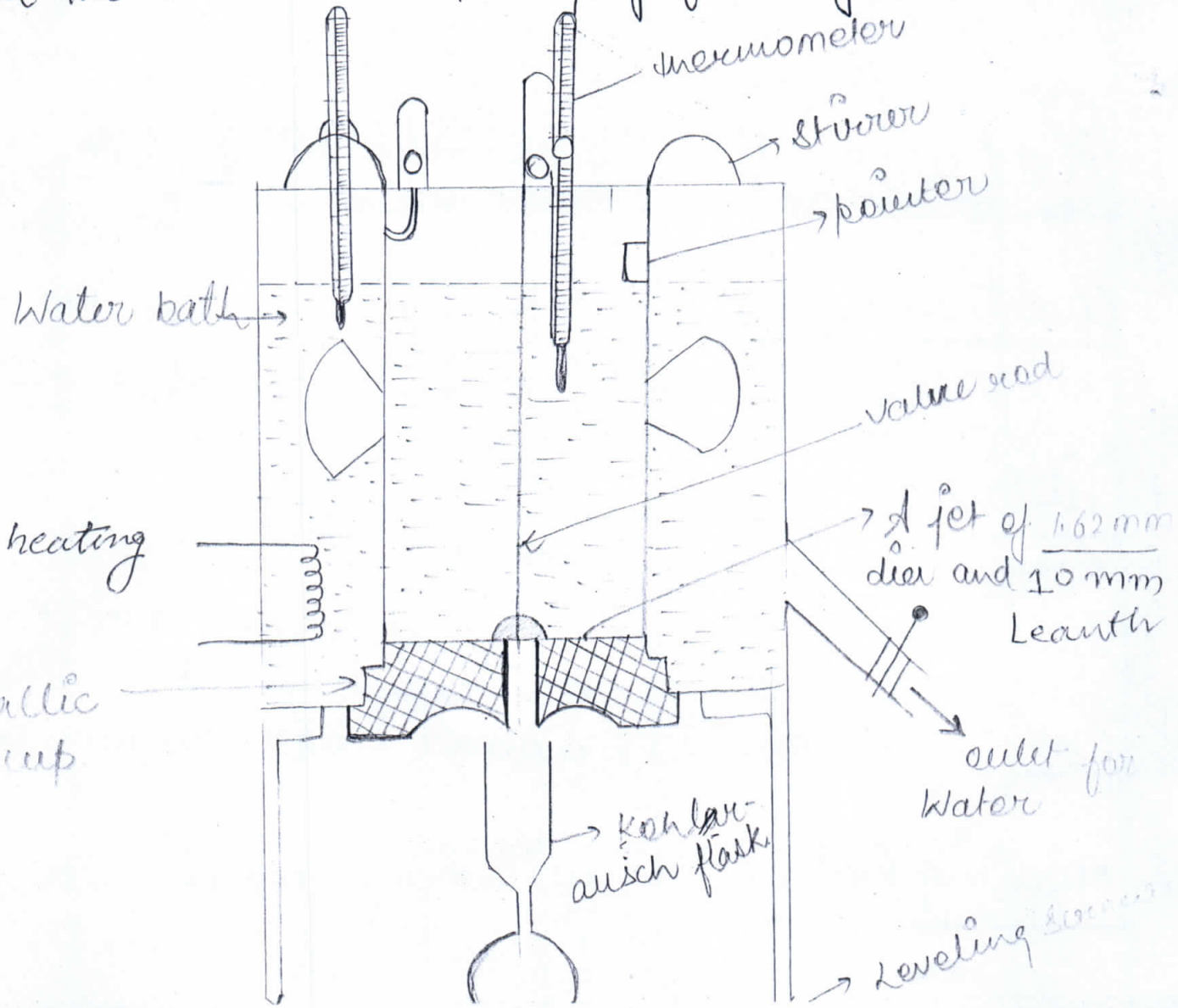
1. **Oil cup :-** cup is a silver plated brass cylinder having height of 90 mm and a diameter of 46.5 mm. The bottom of the cup is with a central hole in which an agate jet with fixed dimension of bore diameter 1.62 mm and length 10 mm is fitted.

2. **Heating Bath :-** A cylindrical copper with containing water surrounds the oil

cup, which is fitted with temp. controlled system and stirring. Heating of water and bath or oil bath can be done either by gas or electric heating.

Spirit Level :- A spirit level used levelling the apparatus vertically is also provided in the lid of the cup. The apparatus is mounted on three legs, provided with levelling screws.

Kohlrausch Flask :- A specially shaped flask known as Kohlrausch flask for receiving the oil from the outlet. The capacity of flask of is 50ml.



Workings :- The viscometer is levelled by adjusting the levelling screws. The water bath is poured in the water bath, upto the indicator mark. The water in the side tube is heated slowly with constant stirring of the bath The Kohlrausch flask is kept set below the set.

The time taken for 50 ml of the oil, to be collected in the Kohlrausch flask is recorded in seconds and the ball value is again placed in the original position. the result is expressed in Redwood NO.-1 Seconds at the particular temp. Higher the time of flow, lesser is the viscosity of oil.

Flash and Fire Points :-

construction :-

Flash point :- The flash point of an oil is lowest temp. at which it gives off vapours that will ignite for a moment when a tiny test flame is brought near it.

Fire point :- The fire point of an oil is the lowest temp. at which the vapours of the oil burn continously for atleast 5 seconds when a time test flame is brought near it.

Construction :-

1. Oil Cup :- It consists of a cup made of brass, which is about 5.5 cm deep and 5 cm is diameter. The lid of the cup is provided with four openings of standard sizes.

2. Shutter :- At top of the cup, a shutter is provided by moving the shutter, opening in the lid opens.

3. Flame Exposure Device :- This device is for introduction of standard flame. Flame exposure device is connected to the shutter in such a way that when shutter is turned, opening of the test flame and air are opened.

4. Air Bath :- The oil cup is holded by its flange, over airbath which is heated by a gas burner or electrically.

Working :- The oil sample filled upto the specific filling mark in the cup and then heated by heating the air bath by a burner, stirrer rotates at a rate of about 1 for 2 revolutions per second Heat is applied, so as to increase the oil temperature by about 5°c per minute.