UNIT-5

ENGINEERING MATERIALS

Cement

Cement is described as a building material which possesses adhesive and cohesive properties to bind rigid masses like stones, bricks, building blocks etc. It possesses the property of setting and hardening when mixed with water to give a paste.

The essential constituents of cement used for constructional purposes are compounds of calcium (calcareous) and Al + Si (argillaceous), materials.

PortlandCement

William Aspdin (1824) is generally recognized as the father of the modern Portland cement industry, as he produced improved cement by heating a mixture of limestone and clay and crushing the resulting product to a fine powder. Portland cement is most widely used non-metallic material of construction. It is also known as 'magic powder' and is a mixture of calcium silicates and calcium aluminates with small amount of gypsum.

The name Portland cement was used because this powder, on mixing with water, sets to give a hard, stone-like mass which resembles the Portland rock.

Raw materials required

a.) Calcareous materials: CaO (such as Limestone, chalk, marl, etc.).
b.) Argillaceous materials: Al_2O_3 and SiO_2 (such as Clay, shale, slate, aluminium ore-refuse etc).
c.) Gypsum: ($CaSO_4.2H_2O$)

Composition of Portland cement

A good sample of Portland cement has the composition of

* Calcium oxide or lime (CaO) = 60 – 70%
* Silica (SiO_2) = 20 – 24%
* Alumina (Al_2O_3) = 5 – 7.5%
* Magnesia (MgO) = 2 – 3%
* Ferric oxide (Fe_2O_3) = 1 – 2.5%
* Sulphur trioxide (SO_3) = 1 – 1.5%
* Sodium oxide (Na_2O) = 1%
* Potassium oxide (K_2O) = 1%
* Gypsum ($CaSO_4.2H_2O$)

During the manufacture of Portland cement, great care should be taken, because

a) Excess lime in cement results in cracks during setting.
b) On the other hand if the lime content is less, the cement is low in strength and sets very soon.
c) Excess silica produces a slow hardening cement.
d) Excess of alumina even though hastens the setting, it weakens the cement.

e) If iron is not present in cement it will be white and hard to burn. The presence of iron imparts a grey colour and also strength to the cement.
f) Presence of excess of alkali oxides causes cement efflorescence.
g) If excess of sulphur trioxide is present, it will reduce the soundness of the cement. (Volume change that takes place when cement is hydrated is called soundness. If volume changes are less then cement is considered to be sound.

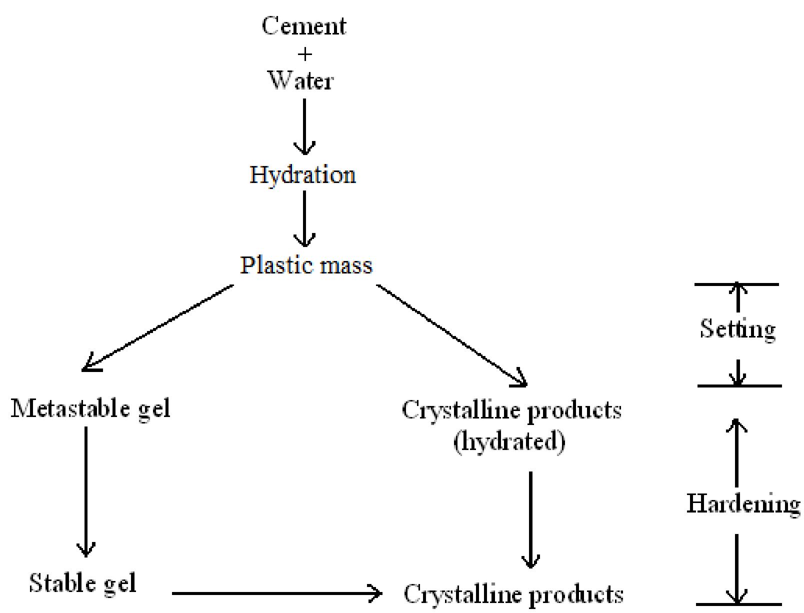
Gypsum helps to retard the setting action of cement. It enhances the initial setting time of cement.

Setting and hardening of cement

When water is added to the cement hydration of cement takes place and a plastic mass called cement paste is formed and then gel and crystalline products.

The process of solidification comprises of i.) Setting and then ii.) hardening

Setting is defined as stiffening of the original plastic mass, due to initial gel formation. Hardening is development of strength, due to crystallization.



Chemical reactions involved in Setting and hardening of cement:

i) Day-1:

When cement is mixed with water, at first, hydration of tricalcium aluminate take place rapidily(within 1 day)and the paste becomes quite rigid within a short time wish is known as intial set or flash set.

$$3CaO.Al_2O_3 + 6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O + 880\ KJ/Kg$$

Tricalcium aluminate **hydrated tricalcium aluminate(crystalline)**

In order to retard the rapid hydration of C_3A, gypsum is added during grinding of cement clinkers.

Gypsum reacts with C_3A to give insoluble calcium sulpho aluminate complex, which does not possess hydrating property and retards early setting of cement.

$$C_3A+3CASO_4.2H_2O \longrightarrow C_3A.3CASO_4.2H_2O$$

ii) Day-2 to7:

Ater the hydration of C_3A,C_3S begins to hydrate to give tobermonite gel and crystalline $Ca(OH)_2$. This is responsible for the development of initial strength of cement. The hydration of C_3S gets completed within 7 days. It does not contribute much to the strength of cement.

$$2(3CaO.SiO_2) + 6H_2O \rightarrow \underbrace{3CaO.SiO_2.3H_2O}_{\textbf{Tobermonite gel}} + \underbrace{3Ca(OH)_2}_{\textbf{crystalline}}+500KJ/kg$$

iii)Day-7 to 28:

Dicalcium silicate reacts with water very slowly and gets completed in 7 to 28 days.

The strength developed by cement paste at any time, depends upon the amount of gel formed and the extent of crystallization.

Initial setting of cement–paste is mainly due to hydration of tricalcium aluminate (C_3A) and gel formation of tetracalcium aluminoferrite.

$$\underbrace{3CaO.Al_2O_3}_{\textbf{Tricalcium aluminate}} + 6H_2O \rightarrow \underbrace{3CaO.Al_2O_3.6H_2O}_{\textbf{hydrated tricalcium aluminate(crystalline)}} + 880\ KJ/Kg$$

$$4CaO.Al_2O_3.Fe_2O_3 + 7H_2O \rightarrow \underbrace{3CaO.Al_2O_3.6H_2O}_{\textbf{Crystal}} + \underbrace{CaO.Fe_2O_3.H_2O}_{\textbf{gels}} + 420KJ/Kg$$

These gels shrink with passage of time and leave some capillaries for the water to come in contact with C_3S and C_2S to undergo further hydration and hydrolysis reactions enabling the development of greater strength over a length of time.

Final setting and hardening of cement paste is due to the formation of tobermonite gel plus crystallization of calcium hydroxide and hydrated tricalcium aluminate.

$$2CaO.SiO_2 + xH_2O \rightarrow \underbrace{2CaO.SiO_2.xH_2O}_{\textbf{Gels}}$$

$$2(3CaO.SiO_2) + 6H_2O \rightarrow \underbrace{3CaO.SiO_2.3H_2O}_{\textbf{Tobermonite gel}} + 3Ca(OH)_2$$

LUBRICANTS

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other. This mutual rubbing of one part over the other leads to resistance of movement, which is termed as friction. Friction usually causes the wear and tear of the machinery, and since heat is generated in this process, it also reduces the efficiency of the machinery. Therefore to overcome the problems created due to friction we employ a substance coined as lubricant. Thus a lubricant may be defined as a substance which reduces the friction when introduced between two surfaces and the phenomenon is known as lubrication.

Characteristics of a good lubricant

Any substance which shows the process of lubrication must satisfy certain key functions. They are:

1. The lubricant should keep moving parts apart.
2. The foremost function of a lubricant is to reduce friction.
3. It should transfer heat and act as a coolant.
4. It should reduce the wear and tear as well as surface deformation caused due to rubbing action of two sliding surfaces.
5. It should prevent rust and corrosion and thereby reducing the maintenance and running cost of the machinery.
6. It should carry away contaminants and debris which would otherwise damage the surfaces of the machinery.
7. It should act as a seal.
8. It should also reduce the loss of energy in the form of heat.
9. It should reduce the expansion of metals due to liberation of frictional heat.

Classification of lubricants

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

1. Lubricating oils or liquid lubricants
2. Greases or semi-solid lubricants and
3. Solid lubricants.

1. Lubricating oils

These lubricating oils provide a continuous fluid film over the moving or sliding surfaces. They also act as cooling or sealing agents, and prevent corrosion.

Eg: animal and vegetable oils, mineral or petroleum oils, blended oils and synthetic lubricant oils.

Animal and vegetable oils: They were used before the advent of industrial revolution and development of petroleum industry. These oils possess good oiliness; they are costly and undergo oxidation easily in the presence of moist air or aqueous medium. They are also useful in the preparation of greases and used as additives to improve lubricating characteristics of petroleum oils. However these are now less preferred.

Examples of vegetable oils: olive oil, palm oil, castor oil, cotton seed oil, etc.

Examples of animal oils: whale oil, seal oil, lard oil, tallow oil, etc.

Mineral or Petroleum oils: They are obtained by fractional distillation of petroleum. They are cheap, quite stable under operating conditions and abundantly available and they replaced the utility of animal and vegetable oils.

Blended oils: Since single oil does not possess all the good qualities of lubrication, certain specific substances (additives) have to be added to achieve the desirable characteristics. This resulted in blended oils.

i.) To improve the oiliness of a lubricant, vegetable oils like coconut oil or castor oil, fatty acids like palmitic, stearic or oleic acid are used as additives.
ii.) To improve viscosity index of lubricants, hexanol is added.
iii.) Organic compounds of phosphorus or antimony are added as corrosion protectives.
iv.) Tricresyl phosphate is added as an abrasive inhibitor.

Synthetic lubricating oils: Since under the conditions of high speed machinery, wide variations in temperature conditions, fire risk and heavy load the petroleum oils cannot be effectively used as lubricants. This led to the development of synthetic oils or lubricants which operate even below -26ºC and above 121ºC.

Eg: Di-basic acid esters, polyglycol ethers, fluoro and chloro hydrocarbons, organophosphates, silicones and silicate esters function as synthetic lubricants.

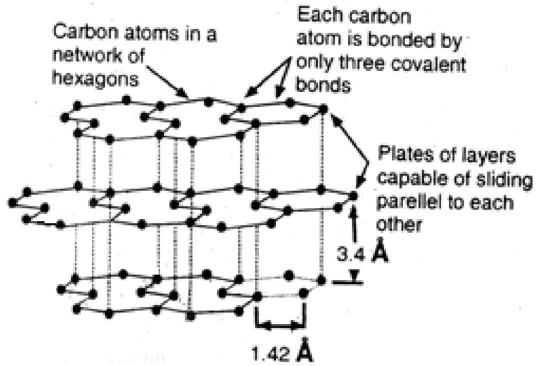
2. Greases or Semi-solid lubricants

A semi-solid lubricant obtained by combining lubricating oil with thickening agent is termed as grease. The thickener is usually sodium, calcium, lithium or aluminium soap. Greases are classified on the basis of the soap used in their manufacture as sodium soap greases (soda-base greases), lithium soap greases, calcium soap greases (lime-base greases), aluminium soap greases and axle greases. Unlike lubricating oils that flow of their own accord, most greases flow only under pressure. Compared to lubricating oils, greases cannot effectively dissipate heat from the bearing. That's why the grease lubricates, bearing works at relatively lower temperatures as compared to the oil-lubricated bearings.

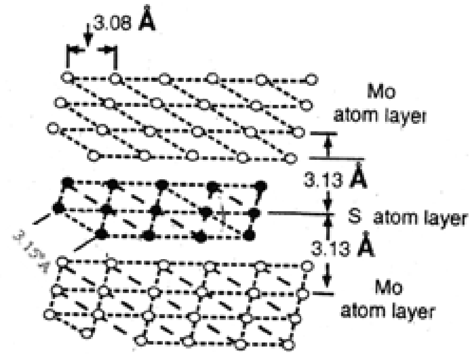
3. Solid lubricants

Oils and greases cannot be used in high temperature and high load conditions and certain other environments. Under such conditions, the solid lubricants are helpful. These are used either as a dry powder form or mixed with oil or water. The commonly used solid lubricants are graphite and molybdenum disulphide.

Graphite is used either as a powder or as a colloidal dispersion in water (aquadag) or in oil (oildag) or as a grease. Colloidal dispersion of graphite is called as dag (deflocculated acheson graphite). Graphite as oil dag is used for lubricating the internal combustion engines and air compressors. Graphite grease which is soapy to touch is used at high temperatures.



Layered structure of Graphite



Sandwich-like structure of molybdenum disulphide

Molybdenum disulphide has a sandwich like structure in which layer of molybdenum atoms lie between two layers of sulphur atoms. This is effective up to 370ºC. Molybdenum disulphide also can be used in powder form or as dispersion in petroleum oils, 2-propanol, water and synthetic oil. It is largely used in air-frame lubrication and wire drawing dyes.

Mixture of graphite (7%), and molybdenum disulphide (70%) bonded with silicates (23%) are capable of withstanding high temperatures, low pressures and nuclear radiations and hence used in space vehicles.

Mechanism of lubrication

There are mainly three types of mechanisms by which lubrication takes place. They are:

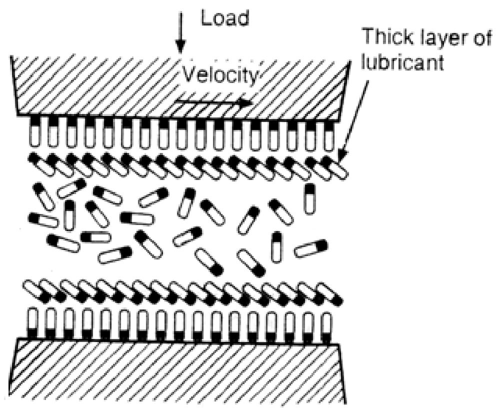
1. Fluid film lubrication or hydrodynamic lubrication
2. Boundary lubrication or thin film lubrication and
3. Extreme-pressure lubrication.

1. **Fluid film lubrication or Hydrodynamic lubrication:** In this type of lubrication, the moving or sliding surfaces are separated from one another by a thick film of lubricant i.e. 1000ºA in thickness, so that there is no direct contact between them. This film also results in covering the irregularities on the moving or sliding surfaces, thereby reducing friction and wear and tear. The coefficient of friction which is a ratio of force required to cause motion to the applied load is as low as 0.001 to 0.03.

   Based on all the above points it is clear that, the fluid film lubrication is based on the properties of the lubricant particularly on its viscosity. This lubrication is satisfactorily done by hydrocarbon oils. These are generally blended with selected long chain polymers in order to maintain the viscosity of the oil as constant in all the seasons.

   The viscosity of hydrocarbon oils increases with increasing molecular weight. Hence, for different applications, appropriate fractions from petroleum refining are blended to meet the requirement. But these fractions generally contain small quantity of unsaturated hydrocarbons which get oxidized under operating conditions, forming gums. Hence it is essential that antioxidants like amino phenols to be blended with hydrocarbon oils.

Light machines like sewing machines, watches, clocks, delicate and scientific instruments are provided with fluid film lubrication.



Fluid-film lubrication

2. Boundary lubrication or thin film lubrication

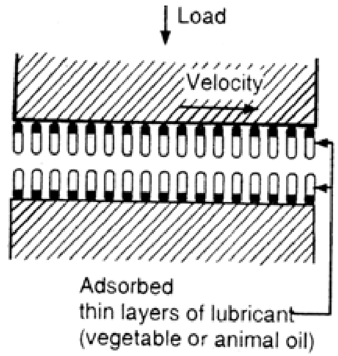
A thin layer lubricant is adsorbed on the metallic surfaces due to physical or chemical forces. This adsorbed layer helps to avoid a direct metal to metal contact between the rubbing surfaces. The load is carried away by the layer of the adsorbed lubricant on both the metal surfaces. This type of lubrication operates when a continuous film of lubricant cannot persist. The coefficient of friction in this case varies from 0.05 to 0.15.

The conditions of the lubricant which ought to be satisfied for boundary lubrication are:

1. Long hydrocarbon chains
2. Polar groups to promote wetting or spreading over the surface
3. High viscosity index
4. Good oiliness
5. Low pour point and oxidation
6. Active functional groups which can form chemical bonds with the metals or other surfaces
7. Resistance to heat, etc.

Solid lubricants, greases and oils with proper additives, function as lubricants in this type of lubrication.

Eg: graphite, MoS_2, mineral oils with additives of fatty acids or fatty oils and vegetable and animal oils and their soaps.



Boundary lubrication

3. Extreme pressure lubrication

Normally under heavy load and high speed operating conditions, a special type of lubricants called high-pressure lubricants are to be employed in order to with stand the high temperatures generated due to frictional heat. In such applications, liquid lubricants fail to stick and may decompose and even vaporize.

Chlorinated esters, sulphurised oils and tricresyl phosphate are examples of such additives. These additives react with metallic surfaces at prevailing high temperatures to form metallic chlorides, sulphides or phosphides, in the form of durable films. These films can withstand very high loads and high temperatures. Hence they serve as good lubricant under extreme-pressure and extreme-temperature conditions.

Extreme pressure additives are used in wire drawing of titanium, in cutting fluids in machining of tough metals, and for hypoid gears used in the rear axle drive of cars.

Properties of lubricants

A study of the various characteristics of a lubricant will help in assessing the suitability of the same for a particular use. The following are some of the important properties normally assessed for lubricating oils.

1. Viscosity:

Viscosity is the property of a fluid or liquid that determines its resistance to flow. A liquid in a state of steady flow on a surface may be supposed to consist of a series of parallel layers moving one above the other. Any two layers will move with different velocities, top layer moves faster than the next lower layer, due to viscous drag i.e., internal friction. Consider two layers of a liquid separated by a distance, d and moving with a relative velocity difference, v. Then, force per unit area, F required to maintain this velocity difference is given by $F = \eta v/d$

where η is a constant of the liquid, called coefficient of viscosity. If v = 1 cm/sec, d = 1 cm, then $F = \eta$.

Hence, coefficient of viscosity (η) may be defined as "the force per unit area required to maintain a unit velocity gradient between two parallel layers". The unit of viscosity is poise. If a force of 1 dyne is required to maintain a relative velocity difference of 1 cm/sec between two parallel layers 1 cm apart, its coefficient of viscosity is 1 poise. A smaller corresponding unit is centipoises, which is equal to 1/100 of poise.

Viscosity is the most important single property of any lubricating oil, because it is the main determinant of the operating characteristics of the lubricant.

i.)If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving or sliding surfaces and consequently, excessive wear will take place. On the other hand,

ii.)If the viscosity is too high, excessive friction will result.

Effect of temperature on viscosity:

Viscosity of liquids decreases with increase in temperature and consequently, the lubricating oils become thinner as the operating temperature increases. Hence, viscosity of good lubricating oil should not change much with change in temperature, so that it can be used continuously, under varying conditions of temperature. The rate at which the viscosity of oil changes with temperature is measured by an arbitrary scale, known as the "Viscosity-index" (V.I.). If the viscosity of an oil falls rapidly as the temperature is raised, it has a low viscosity-index. On the other hand, if viscosity of oil is only slightly affected on raising the temperature, its viscosity-index is high.

Determination of viscosity-index:

A series of two types standard oils, paraffinic-base Pennsylvanian oils (V.I. = 100) and naphthenic-base Gulf oils (V.I. = 0) are used for this purpose. Against each of these, their viscosities are marked at 100°F and 210°F. The former are known as 'H'-oils and the latter as 'L'-oils.

Step-I: The viscosities of oil under test at 100°F and also at 210°F are first found out, let these values be 'u' and 'v' respectively. The difference between the two values should be low, if the oil is good and high, if the oil is poor.

Step-II: Now from the list of H-oils, the oil which has the same viscosity at 210°F as the oil under test is selected, and its corresponding viscosity at 100°F is read off. Let it be H.

Step-III: Then, from the list of L-oils, the oil which has the same viscosity at 210°F as the oil under test is selected, and its corresponding viscosity at 100°F is read off. Let it be L. Then,

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

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

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

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

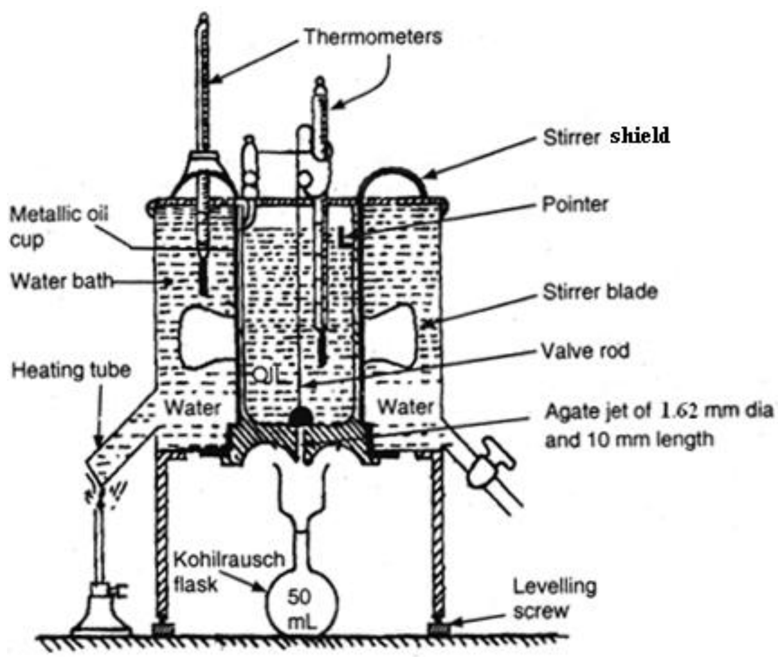
Measurement of viscosity of lubricating oil:

It is made with the help of an apparatus called the 'Viscometer". In a viscometer, a fixed volume of the liquid is allowed to flow, from a given height, through a standard capillary tube under its own weight and the time of flow in seconds is noted. The time in seconds is directly proportional to the true viscosity. Red wood viscometers and Saybolt viscometers are used, respectively in commonwealth countries and U.S.A., for measuring viscosities of lubricating oils. The results are expressed in terms of time taken by oil to flow through particular instrument. For example, if time of flow of an oil through Red wood viscometer at 20ºC is 100 seconds, then its viscosity is "100 red wood seconds" at 20ºC.

Red wood viscometer:

Red wood viscometer is of two types. "Red wood viscometer No.1" is commonly used for determining viscosities of thin lubricating oils and it has a jet of bore diameter 1.62 mm and length 10 mm. on the other hand, "Red wood viscometer No.2" is used for measuring viscosities of highly viscous oils like fuel oil. It has a jet of diameter 3.8 mm and length 15 mm. Red wood viscometer No.1 consists of the following essential parts:

i.)Oil cup: It is a silver-plated brass cylinder (90 mm in height and 46.5 mm in diameter). The upper end of the cup is open. The bottom of the cylinder is fitted with an agate jet (with bore diameter 1.62 mm and length 10 mm). The jet is opened or closed by a "valve rod", which is a small silver-plated brass ball fixed to a stout wire. The level to which the cylinder is to be filled with oil is indicated by a "pointer", which is a stout, tapered, upwards-pointing wire fixed on the inner side of the cylinder. The lid of the cup is fitted with a thermometer, which indicates the oil temperature.



Redwood Viscometer No.1

ii.)Heating bath: Oil cup is surrounded by a cylindrical copper bath, containing water. It is provided with a tap (for emptying water from it) and a long side-tube projecting outwards (for the bath water by means of a gas burner or a spirit lamp). A thermometer indicates the temperature of the water.

iii.) **Stirrer:** Outside the oil cylinder is stirrer, carrying four blades, for stirring the water in the bath for maintaining uniform desired temperature. The stirrer is provided with a circular shield at the top, to prevent any water splashing into the oil cylinder.

iv.) **Spirit level:** The lid of the cup is provided with a spirit level for vertical leveling of the jet.

v.) **Leveling screws:** The entire apparatus rests on three legs, provided at their bottom with leveling screws.

vi.) **Kohlrausch flask:** It is a specially-shaped flask for receiving the oil from the jet outlet. Its capacity is 50 ml up to the mark in its neck.

Working:

The leveled oil cup is cleaned and ball of valve rod is placed on the agate jet to close it. Oil under test, free from any suspension, etc, is filled in the cup up to the pointer level. An empty Kohlrausch flask is kept just below the jet. Water is filled in the bath and side-tube is heated slowly with constant stirring of the bath. When the oil is at the desired temperature, heating is stopped and the ball valve is lifted and suspended from thermometer bracket. The time taken for 50 ml of the oil to collect in the flask is noted and then, the valve is immediately closed, to prevent any overflow of the oil. The result is expressed in “Red wood No.1 seconds” at the particular temperature. Higher the time of flow, higher the viscosity of the oil.

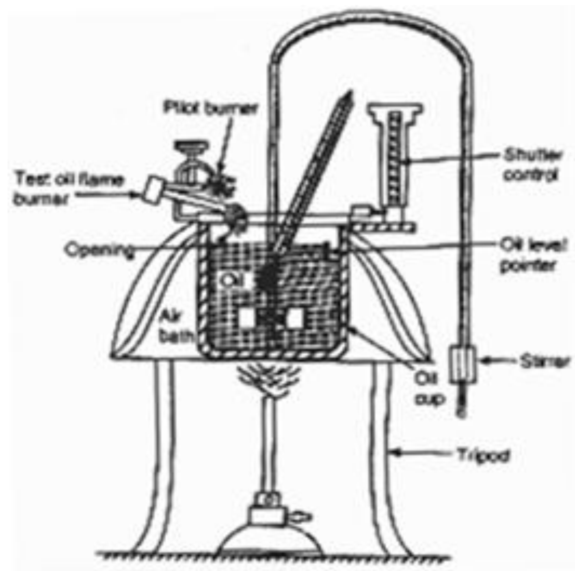
2. Flash and Fire points:

“The lowest temperature at which the lubricating oil gives off enough vapours that ignite for a moment, when a tiny flame is brought near it”; while fire-point is “the lowest temperature at which the vapours of the oil burn continuously for at least 5 seconds, when a tiny flame is brought near it”. In most cases, the fire-points are 5 to 40^{o} higher than the flash-points. The flash and fire-points do not have any relation with the lubricating property of the oil, but these are important when oil is exposed to high temperature service. A good lubricant should have flash-point at least above the temperature at which it is to be used. This safeguards against risks of fire, during the use of the lubricant. The flash and fire-points are, usually, determined by using Pensky-Marten’s apparatus which consists of the following essential parts:

i.) **An oil cup:** It is about 5 cm in diameter and 5.5 cm deep. The level to which oil is to be filled is marked inside the cup. The cup lid is provided with four openings of standard sizes. Through one of these passes a thermometer; while the second opening is used for introducing test flame. Through third opening passes stirrer carrying two brass blades; while the fourth is meant for admission of air.

ii.) **Shutter:** It is a lever mechanism, provided at the top of the cup. By moving the shutter, opening in the lid opens and flame which is carried by a flame exposure device is dipped into the opening, thereby bringing the flame over the oil surface.

iii.) **Flame exposure device:** It is a tiny flame, connected to the shutter by a lever mechanism.



Pensky-Marten flash point apparatus

iv.)Air bath: Oil cup is supported by its flange over an air-bath, which is heated by a gas burner.

v.)Pilot burner: As the test-flame is introduced in the opening, it gets extinguished, but when the test flame is returned to its original position, it is automatically lighted by the pilot burner.

Working:

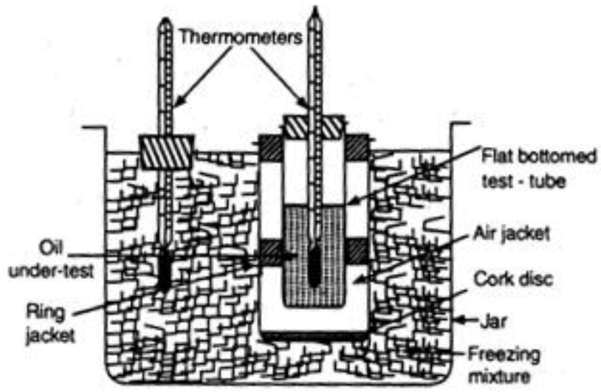
Oil under examination is filled up to the mark in the oil cup and then heated by heating the air-bath by a burner. Stirrer is worked between tests at a rate of about 1 to 2 revolutions per second. Heat is applied so as to raise the oil temperature by about 5°C per minute. At every 1°C rise of temperature, test flame is introduced for a moment, by working the shutter. The temperature, at which a distinct flash appears inside the cup, is recorded as the flash-point. The heating is continued thereafter and the test flame is applied as before. When the oil ignites and continues to burn for at least 5 seconds, the temperature reading is recorded as the fire-point of the oil.

3. Cloud and Pour-points:

When an oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance is called its “cloud-point”; while the temperature at which the oil ceases to flow or pour, is called its “pour-point”. Cloud and pour-points indicate the suitability of lubricants in cold conditions. Lubricant used in a machine working at low temperatures should possess low pour-point; otherwise solidification of lubricant will cause jamming of the machine. It has been found that presence of waxes in the lubricating oil raise the pour-point.

Determination of pour-point:

It is carried out with the help of pour-point apparatus. It consists of essentially a flat-bottomed tube (about 3 cm in diameter and 2 cm high) enclosed in an air-jacket. The jacket is surrounded by freezing mixture (ice+$CaCl_2$) contained in a jar. The tube is half-filled with oil. A thermometer is introduced in the oil. As the cooling proceeds slowly via air-jacket, the temperature falls continuously. With every degree fall of temperature of the oil, the tube is withdrawn from the air-jacket for a moment (about 2-3 sec) and examined. It is then replaced immediately. Temperature at which cloudiness is noticed is recorded as the Cloud-point. After this, cooling is continued and the test-tube is withdrawn after every 3°C fall of temperature and tilted to observe the flow or pour of oil. The temperature at which oil does not flow in the test-tube, even when kept horizontal for 5 secs, is recorded as the pour-point.



Cloud and Pour point apparatus