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ENGINEERING CHEMISTRY (BT-101) NOTES

UNIT III: LUBRICANTS & LUBRICATION**INTRODUCTION:**

All material surfaces, harder or softer, have many irregularities in the form of asperities (Peaks) and valleys. When two solid surfaces are pressed over each other, the asperities of both the upper surface and lower surface come in contact with each other, it causes some deformation effect on the metal surface which is more in case of ductile metals. This contact causes the weld junction which carries all the loads between the two surfaces. Thus, the true area of contact is only a small fraction of the apparent contact area between the two surfaces. Friction is the relative movement of two surfaces in contact with each other. Generally, there are two types of friction encountered, (i) sliding friction and (ii) rolling friction.

Surface wear during sliding is due to shearing of asperities

(i) Sliding friction: The friction caused by the sliding two materials of different hardness over one another. Due to this sliding, the peaks of the softer metal gets broken easily than the peaks of the harder metals.

The effects of the sliding friction are:

- (a) Ploughing i.e., cutting out the softer material by the asperities of the harder materials.
- (b) The interlocking of the surface irregularities.

(ii) Rolling friction: It occurs when a load sphere or cylinder rolls over a flat surface of the other body. The coefficient of the rolling friction is usually very low as compared to the sliding friction. Thus, the effect of rolling friction is much lower than the sliding friction, as the effect of rolling friction is caused by elastic deformation of the two surfaces. In case of sliding friction, the coefficient of friction is much larger in static condition than for the kinetic condition. Therefore, the lubricant plays less important role in case of rolling friction than the sliding friction.

In case of any friction a considerable amount of frictional heat is released at the rubbing surfaces which is more in case of sliding friction as the contact area of this friction is more. The frictional heat is not uniformly distributed over apparent contact area between the rubbing materials but it is highly localized, particularly at the surface asperities. If this frictional heat reaches the melting temperature of the material, welded junction may be formed. The amount of frictional heat depends upon the nature of the sliding material and the speed of the sliding.

Lubricant- A substance which is introduced between two relatively moving surfaces for reducing friction and wear is called lubricants. The process of reducing frictional resistance between moving surfaces by the application of lubricants is called lubrication.

Functions of Lubricants:

1. It reduces the loss of energy in the form of heat.
2. It increases the efficiency of machine.
3. It efficiently prevents the interlocking or inter-joints welding at the surface asperities.
4. It increases the smooth motion of the moving parts.
5. It reduces the surface deformation, wear and tear.
6. It reduces the expansion of metal by local frictional heat.
7. It protects the materials from corrosion.
8. Sometimes it stops the leakage of gases or pressures from the cylinder.

Mechanisms of Lubrication:-

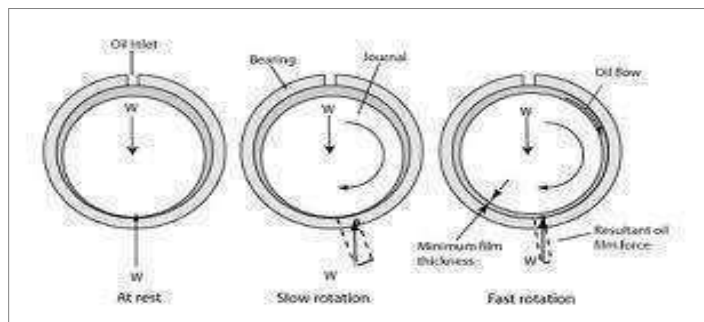
There are mainly three types of mechanism of lubrication. They are:

1. **Fluid film or hydrodynamic lubrication.**
2. **Thin film or boundary lubrication.**

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3. Extreme pressure lubrication.

(1) Fluid film or hydrodynamic lubrication: In this lubrication, two moving surfaces are separated from each other by a thick film of lubricating oil O (thickness around 1000\AA). Hence it prevents the direct contact between these rubbing surfaces and welding of junctions generally does not occur. This happens because, the lubricating oil cover the irregularities of the Sliding surfaces & forms a thick layer in between them, so that there is no direct contact between the material surfaces. Actually the shaft floats in the lubricant.



The resistance to movement of moving parts is only due to the internal resistance between the particles of the lubricant moving over each other. Based on this principle, the lubricant chosen should have low viscosity. Selection of lubricant: In order to maintain a suitable viscosity of the oil, ordinary hydrocarbon lubricants are blended with long chain polymers. At operating condition, hydrocarbon petroleum fractions. Generally contain small quantities of unsaturated hydrocarbons, which get oxidized to form gummy products. To reduce the antioxidants like amino phenols are added. This type of hydrodynamic lubrication gives satisfactory results as the coefficient of friction in such cases is very low. Hydrodynamic friction occurs in the case of a shaft running at a fair speed with a low load.

(ii) Boundary lubrication or thin film lubrication: It is done when a thick fluid film cannot be maintained between the two moving surfaces so that direct metal to metal contact is possible. This happens when (i) the viscosity of the oil is low (ii) the load is very high (iii) the speed of the movement is very low and (iv) a shaft starts moving from rest. Under such conditions, the lubricant should be adsorbed physically or chemically on both the metallic surfaces. These adsorbed lubricant layers avoid the direct metal to metal contact. The coefficient of friction in these cases is slightly more than hydrodynamic lubrication. In boundary lubrication, surface asperities contact each other even though the lubricant supports much of the load. Friction depends mainly on the shearing forces necessary to cleave these adhering asperities and wear and friction can be reduced by certain additives. Wear inhibitors and lubricity agents are polar materials that adsorb on a metal and provide a film that reduces metal-to-metal contact.

Condition of lubricants: The lubricant used for boundary lubrication should have:

- (1) Long hydrocarbon chains.
- (2) Lateral attraction between the chains.
- (3) Polar groups to promote spreading and orientation over the metallic surfaces at high pressure.
- (4) Active groups to form chemical bonds with metallic surfaces.

In this boundary lubrication the metal surfaces are closer to each other, but still they are well separated by the lubricant. The property of the oil which enhances the adsorption and maintenance of the thin film is called oiliness. High viscosity index, resistance to heat and oxidation, good oiliness and low pour

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point are some of the good qualities of boundary lubricants. Boundary lubrication (i.e., the boundary friction) boundary lubrication is the lubricant from the friction surfaces between the molecules and the internal friction between molecules (i.e., liquid lubrication) the transition to direct contact with the surface friction before the critical state. At this time there is a layer of friction interface adsorption film thickness is typically about $0.1\mu\text{m}$, with some lubrication. We call this layer of thin boundary film. Boundary lubrication film depends on the nature of the friction surface; depends on the oil lubricant additives, extreme pressure additives on the friction surface of the metal structure of the boundary film formation with the oil viscosity has little mouth. Generally vegetable and animals oils have all the above mentioned good qualities of lubricant. They are adsorbed (physically or chemically) easily on the, metal surfaces with the active group of $-\text{COOH}$. But they tend to break down at high temperatures. In order to improve the oiliness of the mineral oils, usually little fatty acids are added.

(iii) Extreme pressure lubrications: Extreme pressure lubrication are a special case of boundary lubrication, friction is Deputy Commissioner in the override (or high contact stress), speed, temperature conditions, extreme pressure lubricant additives react with the metal friction surface generate a chemical reaction film, separated the two friction surfaces, and play a lower coefficient of friction, reduce wear and tear (or change the direct contact with the metal surface of serious wear and tear), to the role of lubrication, it is called extreme pressure lubrication. When the moving surfaces are under very high pressure and speed, the lubricant may decompose or vaporize or they may not stick on the surfaces because high local temperature is produced. To meet these extreme pressure conditions, special additives called "extreme pressure additives" are added to the mineral oils. Extreme pressure additives are compounds having active groups such as chlorine (chlorinated esters), sulphur (sulphurised oils) and phosphorus (tricresyl, phosphate). At high temperatures, they react with metal giving surface layers like metallic chlorides, sulphides or phosphides. These surface layers have high melting point and serve as good lubricant under extreme pressure and temperature conditions. Extreme pressure (EP) additives are a special class of boundary lubrication additive which react with the metal surface to form compounds with lower shear strength than the metal.

Classification of Lubricants:-

Lubricants may be broadly classified, on the basis of their physical state as:

1. Liquid Lubricants.
 - (a) Vegetable oils and animals oils.
 - (b) Mineral oils from petroleum.
 - (c) Blended oils or doped oils or compound oils.
 - (d) Synthetic oils.
2. Semi solid lubricants.
3. Solid lubricants.

Lubricating Oils/ Liquid lubricants:

(a) Vegetable or animal oils: These are most commonly used lubricants. They possess good oiliness and adsorb themselves on the metallic surfaces. However, they decompose at high temperatures and undergo oxidation easy, forming gummy and -acidic hydrolyzed products and get thickened on coming in contact with air. Thereby restricting the smooth movement of the moving surfaces. To overcome such restrictions, usually they are blended with mineral oils (blending agents).

(b) Mineral oils: They are obtained by fractional distillation of petroleum. They are the heavier fractions containing long chain hydrocarbons in petroleum oils ranging between 12 to 50 carbon atoms. The shorter chain oils have lower viscosity than the longer chain hydrocarbons. They are widely used as

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lubricants as they possess good stability under service conditions but poor oiliness. The oiliness of these oils can be improved by adding oils like oleic, stearic acids etc. They have impurities like sulphur compounds, gum forming alkenes, asphalt, waxy impurities, other color impurities, reluctant and some other unwanted impurities. All these impurities should be removed to prevent the formation of corrosive and gummy products to decrease the friction.

Removal of impurities: A number of processes are used for removing these undesired impurities as follows:

(i) Solvent refining: Sulphur compounds, alkenes and other gum products can be removed by this process. In this process, the oil is mixed with a suitable solvent like phenol which is immiscible with oils. But the undesirable impurities are highly soluble in phenol, thereby the liquid separates into two layers (oil goes up and phenol comes down).

Oil layer is free from impurities but containing some solvents and the solvent layer contains the impurities. Then the oil layer is distilled out and some additives may be added to improve the lubricating quality of the oil.

(ii) Dewaxing: Waxy impurities are removed by treating the lubricants with suitable solvents like propane and then the wax solution is cooled. The wax precipitates, which is removed from the oil by passing the oil wax suspension through a filter. The solvent present in the oil is then recovered by distillation.

(iii) Filtration: The colored impurities can be removed by filtration through bauxite or clay.

(iv) Acid refining: Sometimes the dewaxed oils contain a number of undesirable impurities. To eliminate these impurities, the dewaxed-oil is treated with concentrated H_2SO_4 and then agitated so that the impurities dissolve in acid and it is filtered out. This filtrate is neutralized by adding a calculated amount of a base NaOH.

(c) Blended lubricating oils: Single oil cannot possess all the good qualities of the lubrication. Therefore to get the satisfactory lubricant with desirable characteristics, specific additives are blended with the oil. These are called blended oils. An additive is a material that imparts a new or desired properties to the lubricating oil. It may also enhance a desirable property that the lubricating oil already possess to some degree. Broadly, there are two types of additives chemically active additive & chemically inert additives. Chemically active additive are those which chemically interact with metals (to form protective films) dispersant, detergents, extreme pressure agents, etc. Chemically inert additives are those additives which improve the physical properties that are critical to the effective performance of the lubricant. Like viscosity index improver, foam inhibitors etc.

Greases or Semi solid lubricants:-

The most important semisolid lubricants are Greases and Vaseline.

Grease: Grease is used to lubricate journal bearings when cooling of the bearing is not a factor, typically if the bearing operates at relatively low speeds. Grease is also beneficial if shock loading occurs or if the bearing frequently starts and stops or reverses direction. Grease is almost always used to lubricate pins and bushings because it provides a thicker lubricant than oil to support static loads and to protect against vibration and shock-loading that are common in many of these applications. Lithium soap or lithium complex thickeners are the most common thickeners used in greases and are excellent for most journal bearing applications.

Grease is a semisolid combination of a petroleum product and soap. It is obtained by saponification of fat (fatty acids etc.) with alkali like NaOH followed by adding hot Lubricating oil under agitation. The amount of mineral oil added determines the consistency of the finished grease. Soaps are gelling agents which can interconnect with the added oil. Therefore, the structure of the lubricating greases is like gel.

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Soaps dissolve in the oil at higher temperatures so that the interconnecting bonds will be broken out and the grease liquefies. To improve the heat resistance of grease; inorganic solid thickening agents like clay, colloidal silica, carbon black etc. are added to it.

Advantages of greases:

1. Greases have higher frictional resistance than oil.
2. Because of the presence of soap in oil, greases stick well on the surfaces.
3. Greases are used in situations where oil film cannot be remaining in its position i.e. in machine working under high pressures at slow speed.
4. Greases can support heavier load at low speed.
5. Greases can be used in bearing and gears that work at high temperatures.
6. They are used in situations where sealing is necessary against entry of dust, dirt, grit or moisture.
7. Greases are used in situations, where dripping or spurting of oil is undesirable; therefore it can be used in textile and good products manufacturing industries.
8. They also do not require much attention as oils.

Disadvantages of greases:

1. They have high co-efficient of friction.
2. They have a tendency to separate into oils and soaps. .
3. On long use, oil in the grease may evaporate.
4. Greases cannot effectively dissipate heat from the bearing.

Greases are classified based on the soap used in their manufacture as below:

(a) Lime or calcium soap grease or cup greases: They are the emulsions of petroleum oil with calcium soaps. They are insoluble in water, so water resistant. Above 65°C they cannot be used because oil and soap separates out above this temperature. They are widely used as they are the cheapest.

(b) Sodium soap greases: They are sodium soaps dispersed in petroleum oils. They are water soluble, so they are not water resistant. They can be used up to 175°C because of its high melting point and fibrous structure. They are suitable for use where the lubricants get heated due to friction.

(c) Lithium soap greases: They are petroleum oils, thickened by mixing lithium soaps. They are water resistant, high temperature withstanding, good mechanical stability and low oxidation tendency. They are suitable for use at low temperature about 15°C only. They are used in multipurpose.

(d) Aluminum soap greases: They are aluminum soaps dispersed in oils. Due to its low soap content, they are water proof. They cannot be used above 90°C .

(e) Axle greases: They are the resin greases. They are separated by adding slaked lime to the mixture of soluble resin oil and fatty oils. They are allowed to react at 58°C . The mixture is thoroughly mixed and allowed to stand, when grease flats as stiff mass called cold set grease. Filters like talc and mica are also added to these greases. They are water resistant and suitable for use as axle greases and for heavy equipments.

Solid Lubricants: Solid lubrication between the friction surface materials into the solid lubricant powder also can play a good lubricating effect. Friction between the two surfaces of solid lubricant, its shear resistance is very small, slight external force, will have a slip between molecules. This put the two outside the friction between the grinding into a solid lubricant in friction between molecules. There are two necessary conditions for solid lubricant, the first is a solid lubricant molecules should have a low shear strength, it is easy to slip; followed with solid lubricant to the friction surface has a strong affinity, in the friction process, always has maintained that the surface friction layer of solid lubricant, and a layer of solid lubricant which does not corrode the surface friction. Generally attached to the metal surface, a mechanical, but there are also form a chemical combination. The nature of the solid material with many, such as graphite, molybdenum disulfide, talc and so on. For non-layered structure for the

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solid lubricant, or soft metal, mainly for its low shear stress, play a role of lubrication, then it attached to the friction surface lubricating film. For the already formed solid lubricating film lubrication mechanism of boundary lubrication mechanism can explain the lubrication approximation.

The two most usual solid lubricants employed are graphite and molybdenum disulphide. These lubricants are used either in the dry powder form or mixed with water or oil. The solids fill up the low spots in the surfaces of moving parts and form solid films, which have low frictional resistance. The usual coefficient of friction between solid-lubricants is between 0.005 and 0.01.

Advantages of solid lubricants:

1. They are used in heavy machineries working at very high loads and slow speeds.
2. The operating temperature is too high.
3. Liquid lubricants and greases are easily contaminated with dust which is unaccountable, for example, in commutator blades of electric motors and generators, because proper films cannot be maintained.
4. Combustible lubricants must be avoided.

1. Graphite: Graphite is most widely used of all solid lubricants. In graphite, carbon atoms are arranged in hexagons in several flat layers, which are held together by only weak bonds so that the force to shear the crystals parallel to the layers is low.

Each carbon atom in a layer is surrounded by three other carbon atoms.

Lubricating action of graphite: It is very soapy, non flammable graphite is mainly used at high temperature in the absence of air and high pressures. Graphite is used either in dry powder form or dispersed in oil (oil dag) or in water (aqua dag) or as graphite grease. Oil dag is found particularly useful in IC engines, because it forms a film between the piston rings and the cylinder and gives a tight fit contact, thereby increasing compression. Water dag is used in food industries, where a lubricant free from oil is needed. Graphite grease is used at high temperature.

Uses: It is used as lubricant in air compressors, lathes, general machine-shop works, food stuffs industry, railway track joints etc.

2. Molybdenum disulphide: It has sandwich like structure 'Mo' and 'S' are separately arranged in different layers and are sandwiched alternatively.

Lubricating action of molybdenum disulphide: Poor inter laminar attraction is responsible for low shear strength in a direction parallel to the layers. It is stable up to 400°C and is used at high temperatures. It possesses very low coefficient of friction. It can be used as a dry powder or oil-dag or aqua-dag or grease. A solid film made from 70% MoS₂, 7% graphite and 23% silicate is used in space vehicles which can withstand high temperature and even nuclear radiation. The other commonly used solid lubricants are talc, mica, soap stone etc. Teflon acts as a lubricant in gear pumps, periscope etc.

Synthetic Lubricants: These are synthesized specially to meet the severe operating conditions. The synthetic lubricants can perform well over a wide range of temperatures from -50°C upto 260°C. These lubricants possess low freezing points, high viscosity index and non flammable. Polyalkene glycols, silicones, chlorinated and fluorinated hydrocarbons; organic amines, imines and oxides are the important synthetic oils.

Advantages of synthetic lubricants

1. They possess high thermal stability at high operating temperatures.
2. They have viscosity index and high flash points.
3. They are chemically stable and having low freezing points.

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(a) **Polyalkene glycols:** Polyalkene glycols like polyethylene glycol, poly-propylene glycol etc. can be used as both water soluble and water insoluble lubricants in rubber bearings and joints. They have all the three advantages mentioned above.

(b) **Silicones:** These synthetic lubricants are not oxidized below 200°C and possess high viscosity index. At temperature above 200°C , silicones are oxidized quickly and undergo cracking process at about 230°C . Therefore such lubricants are used for low temperature lubrication purposes but not employed for high temperature applications.

(c) **Chlorinated and fluorinated hydrocarbons:** They are not decomposed by heat, not easily oxidisable and chemically inert and resistant to chemicals etc.

(d) **Organic amines:** They are good synthetic lubricants, since they possess low pour points and high viscosity index. They can be used under temperature conditions of -50°C to 250°C .

Lubricating Emulsions: - An emulsion is a heterogeneous system consists of disperse phase and dispersion medium. In this emulsion, the two phases are immiscible liquids. The liquid being dispersed as fine droplets (dispersed phase) into a fairly coarse dispersion medium. The size of dispersed phase should be within the range of 1 micron to 6 micron. As the two immiscible liquids is inherently unstable, it is prepared by vigorous stirring and addition of emulsifier or emulsifying agent to make it more stable. The emulsifying agents contain polar and non- polar groups and they are classified as hydrophilic end and hydrophobic end depending on their affinity towards water molecule. The hydrophilic end emulsions have greater affinity towards water while the hydrophobic ends do not have any affinity towards water, rather they are preferred to wet by oil. The emulsifier molecule is adsorbed at the interface of the two phases, resulting in formation of a protective film around the dispersed droplet. For example, soaps of different types, detergents, long chain sulphonic acids, lyophilic colloids etc. act as emulsifying agents in different cases. A certain large number of droplets of a liquid into another liquid increases the surface area and hence requires large amount of energy. The required energy would be less if the surface tension is decreased. The function of the emulsifying agents is to diminish the surface tension.

Emulsions are broadly classified into two types (1) Oil in water type in which the disperse phase is the oil in water medium (2) Water in oil type in which water droplets are dispersed in oil. The type of emulsion produced depends upon the nature of the emulsifying agents used. For example, when sodium oleate is used as an emulsifier, oil in water emulsion is formed. But if soap with a bivalent cation is employed, say calcium oleate, water in oil type emulsion is obtained. In order to ascertain the type of given emulsion, a small quantity of water is added with stirring and the effect is observed under a microscope. If the emulsion is oil in water type, water would mix freely with the excess medium, the droplets remaining undisturbed. If it is water in oil type, the addition of oil to the emulsion would produce similar effect.

Properties and Testing of lubricating oils

1. Viscosity and Viscosity index
 2. Flash Point and Fire Point
 3. Cloud Point and Pour Point
 4. Aniline Point
 5. Steam Emulsion Number
 6. Neutralization Number
 7. Saponification Number
 8. Iodine value
 9. Carbon residue
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1. VISCOSITY: - It 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.

Absolute viscosity may be defined as "the tangential force per unit area which is required to maintain a unit velocity gradient between two parallel layers; It is denoted by η . Its unit in C.G.S. System is poise and its dimensions are $ML^{-1}T^{-1}$

Absolute Kinematic viscosity is the ratio of absolute viscosity to 'density for any fluid. It is denoted by ν . Its unit in C.G.S. system is stokes and its dimensions are L^2T^{-1}

Effect of temperature on viscosity.

Like any other fluid, viscosity of lubricating oil is inversely proportional to temperature. *i.e.*, with increase of temperature, viscosity decreases. This is due to the decreases in intermolecular attraction. At higher temperatures oils must have sufficient viscosity to carry loads. Hence, heavier oils are used at higher temperatures. Similarly, light oils are used at low ambient temperatures.

Effect of pressure on Viscosity

Lubricating oils are subjected to extreme pressure at the interface between gears and between rolling element and race in a rolling bearing.. At such high pressures, viscosity of lubricating oils increases considerably.

Significance of Viscosity.

Viscosity helps in the selection of good Lubricating oil. For instance, Light oils have low densities and easy flowability. These oils *i.e.*, generally used on parts moving at high speed promotes the formation of a good oil film. Moreover, light oils do not impose much drag on high-speed parts.

Diagram (from manual):

In contrast, Heavy oils are used on parts moving at slow speed under heavy loads as they resist being squeeze out. Light oils are not suitable in this case as they have low viscosities and it is not possible to maintain lubricant film between the moving surfaces. Subsequently, excessive wear will occur. To sum up, in hydrodynamic lubrication, that lubricant is selected which should have a sufficient high viscosity to adhere to the bearing and resist being squeeze out due to high pressure and get fluid enough to resist excessive friction due to the shearing of oil itself. Thinner oil can easily dissipate the frictional heat because of good oil circulation.

Measurement of viscosity of lubricating oil

There are many instruments for measuring viscosity and are known as viscometers (or viscosity meters). For examples, Kinematic & Saybolt universal viscometers used in the United States and the Redwood viscometers are commonly used in England.

The Saybolt Viscometer

It consists of cylindrical brass cup in the bottom of which is an orifice of specified dimension. This cup is surrounded by constant temperature oil bath. A desired bath temperature can be obtained by adjusting the temperature regulator. When the sample of lubricating oil reaches test temperature. The time required for 60 mL of the oil to run through the orifice is measured. The oil sample flow by gravity under a standard falling head and at a temperature of 100°F and 210°F. A calibrated standard flask collects the liquid sample. The time of efflux is measured in seconds and are reported as Saybolt Universal Seconds (SUS); for example, 260 SUS, at 100°F. For heavy lubricating oils with high viscosities, a large orifice is used in the same apparatus, and the results are reported in Saybolt Furol Seconds (SFS) at a Specified temperature.

The kinematic Viscometer

It is a U-type of glass apparatus having respectively cone and two bulbs at its two sides. At the bottom portion of two bulb side, capillary tube is attached. It is used for the determination of Kinematic

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viscosity. The four simple measurements steps are shown. For a fixed volume of sample, time is measured for the sample to flow through a calibrated capillary under an accurately reproducible head of liquid and at a constant temperature. From the measured efflux time, the kinematic viscosity is calculated.

$$\text{Kinematic viscosity in centistokes (CST)} = C \times t$$

Where C = Viscometer constant and.

t = Observed flow time in seconds.

The Redwood Viscometer: It is of two types:

(a) Redwood viscosity No. 1-Universal and (b) Redwood viscosity No.2-Admiralty.

The essential differences between the two are:

	(a)	(b)
Dimensions of Orifice.	Length: 10 mm Diameter: 1.62 mm	50 mm 3.80 mm
Useful for	Low viscous oils	Higher viscous oils
Receiving flask has	Smaller mouth	Larger mouth

The Redwood No. 1 apparatus consists of a cylindrical brass oil cup (90mm in height and 46.5 mm in diameter) that holds the test sample of lubricating oil. Bottom of the oil cup is fitted with a polished-agate discharge tube containing an orifice of specified dimension. The oil cup is surrounded by water bath for adjusting the temperature. A calibrated receiving flask (known as Kohlrausch flask) is provided for receiving the oil from polished-agate discharge tube. It is shown in when the sample reaches test temperature the time for 50mL of the sample flow through the orifice is measured. Results are reported in seconds.

For example, Redwood Viscosity No. 1 at 140°F, 350 seconds.

Conversion Formulas:

Let time of efflux = t seconds,

Saybolt: $cSt = 0.22 t - 180ft$

Redwood: $cSt = 0.26 t - 171ft$.

Significance of viscosity measurements.

Viscosity is the property of lubricating oil that determines its ability to lubricate. Viscosity values are used in evaluating load carrying capacity, in denoting the effect of temperature changes, for establishing uniformity in shipments and for determining the presence of contaminants in used oil during absolute Viscosity values are required for use in all-bearing design calculations and other lubrication Engg. Technical design problems. Kinematic values are applied in oil blending procedures.

Viscosity Index -With changes in temperature, the viscosity of lubricating oil varies, the higher the temperature, the lower the viscosity and vice-versa. The rate of variation of Viscosity with temperature is different for different base oils or fluids. For example, in petroleum oils, the viscosities of naphthenic base oils vary more over the same temperature range than those of paraffinic base oils. The rate at which the viscosity of oil changes with temperature is measured by an empirical number, known as the **viscosity-index (V.I.)**. A relatively small change in viscosity with temperature is indicated by high viscosity index. Whereas a low viscosity index shows a relatively large change in viscosity with temperature. The Pennsylvanian oils, consisting mainly of paraffin's, are arbitrarily assigned a viscosity index value of 100 as they exhibit a relatively small change in viscosity with a rise in temperature. Oils of Gulf-coast origin, consists mainly of alicyclic (naphthenic), and are arbitrarily assigned a viscosity index value of 0 as they exhibit a larger change in viscosity with a rise in temperature. In industry, lubricating oils of high viscosity index are preferred since they have practically the same viscosity over a range of temperatures. Determination of Viscosity-index, Viscosity index of test oil is determined with

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the help of two types of standard oils viz. Pennsylvanian oils and Gulf oils having V.I.'s 100 and 0 respectively. The V.I. of the test oil is given by the formula:-

$$\text{V.I.} = L - U / L - H \times 100$$

V.I. = viscosity index of the oil under-test.

L = viscosity at 100° F of the low-viscosity standard oil having a V.I. of a (i.e., Gulf oil) and also having the 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 Viscosity of 100 (i.e., Pennsylvanian oil) and 50 having the same viscosity as the oil under test 210° F.

Example 1. *An oil of unknown viscosity-index has a Saybolt universal viscosity of 60 seconds at 210° F and of 600 seconds at 100° F. The high viscosity index standard (i.e Pennsylvanian) oil has Saybolt viscosity of 60 seconds at 210° F and 500 seconds at 100° F. The low viscosity-index standard (i.e., Gulf oil has a Saybolt universal viscosity*

6? Seconds at 210° F and 800 seconds at 100° F. Calculate the viscosity index of unknown oil.

Solution. Here $L = 800$ s, $H = 500$ s and $U = 600$ s

So, viscosity-index of unknown oil $\text{V.I.} = L - U / L - H \times 100$

$$800 - 600 / 800 - 500 \times 100$$

$$\text{V.I.} = 66.67$$

Example 2. *An oil sample under test has a Saybolt universal viscosity of 64sec.at 210° F and 564 seconds at 100° F. The low viscosity standard (Gulf oil) possess Saybolt ,viscosity of 64 seconds at 210° F and 774 seconds at 100° F and 414 sec. at 100° F. Calculate the viscosity-index of the oil sample under test.;* Solution. Here, $L = 774$ s, $H = 414$ s and $U = 564$ s

So, viscosity index of the oil-sample. Under test, $\text{V.I.} = L - U / L - H \times 100$

$$= 774 - 564 / 774 - 414 \times 100$$

$$\text{V.I.} = 774 - 414 \times 100 = 58.33$$

Viscosity Index and Molecular Structure of Oil

There is a direct co-relation between molecular structure of lubricating oil with its viscosity and viscosity-index. A high V.I. is exhibited, by those lubricating oils which have linear or rod-like shaped molecules of higher molecular weights. This is due to the greater inter-molecular attraction.

Viscosity-Temperature Curves.

The variation of viscosity with temperature can also be indicated by viscosity- temperature curves: In fact, viscosity index is the numerical expression of the average slope of the viscosity-temperature curve of lubricating oil between 100°F and 210° F. Lubricating oils with small variation in viscosity with temperature exhibit flatter viscosity-temperature plots and they have high VIs.

GRAF (from manual)

1. Flash and Fire & Point:

The *flash point* of oil is the lowest temperature at which it gives off vapors that will ignite for a moment when a small flame is brought near it. The *fire point* of oil is the lowest temperature at which the vapors of the oil burn continuously for at least 5 seconds when a small flame is brought near it.

The flash points and fire points are used to indicate the fire hazards of petroleum products and evaporation losses under high temperature operations. Knowledge of flash and fire points in lubricating oil aids in precautionary measures against fire hazards. A good lubricant should have flash point at least above the temperature at which it is to be used.

Measurement of Flash and Fire Points of Lubricating Oil

(i) *The Pensky-Marten Closed cup method.* It is used to determine- the flash Point of lubricating oils, fuel oils, solvents, solvent containing materials and suspension of solids, except cut-back asphalt. It consists of a *cup* made of brass, which is about 5.5 mm deep and 5 cm in diameter. The lid of the cup is provided with four openings of standard sizes. Through one of these openings passes a *stirrer* carrying

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two brass blades; while the second opening is meant for admission of air. Through third opening passes a thermometer. While the fourth is meant for introducing test flame. At the top of the cup, a *shutter* is provided. By moving the shutter, opening in the lid opens and flame (from *flame exposure device*) is dipped into this opening. There by bringing the flame over the oil surface. 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. There is also a stove consisting of an air bath and a top plate on which the flange of the cup rests. The air bath may be either a flame-heated metal casting or an electric-resistance element. Pensky-Marten's flash point apparatus is shown in Fig. **DIGRAM (from manual)**

Procedure. The oil sample is filled up to the specified filling mark in the cup. It is then covered and positioned properly in the stove. The thermometer is inserted in the sample. The test flame is lighted, while being stirred, the sample is heated at the rate of 9° to 11°F per minute. Upto 220°F , the test flame is applied at every 2°F rise in temperature, thereafter it is applied at every 5°F rise in temperature. When a distinct flash occurs in the interior of the cup at the time of the flame application, the temperature reading on the thermometer is the flash point.

2. Cloud and Pour Points.

The **cloud point** of petroleum oil is the temperature at which solidifiable compounds, like paraffin wax, present in the oil begin to crystallize or separate from solution. When the oil is cooled under specified conditions. Naphthenic type of oils that are quite wax-free show no cloud points. The **pour point** of a petroleum oil is the temperature at which the oil ceases to flow or pour.

At the Cloud point, oil becomes cloudy or hazy in appearance. Cloud and pour-points indicate the suitability of lubricants in cold conditions. Lubricants used in a machine working at low temperature should possess low pour-point; otherwise solidification of lubricant will cause jamming of the machine. Pour point is of importance in establishing the lowest temperature at which a diesel fuel is still sufficiently fluid to be pumped or transferred. Oil with a low pour point should be selected whenever the oil must remain fluid at low temperatures.

Determination of cloud and Pour Points- These determinations are carried out with help of apparatus. The apparatus consists of a flat-bottomed tube (about 2 cm high and 3 cm in dia.) enclosed in an air-jacket. The air-jacket is surrounded by freezing mixture. (Ice + NaCl) contained in a jar.

To determine cloud point, a sample of the lubricating oil (moisture free) is poured into a test jar and cooled in progressive steps. When inspection first reveals a distinct cloudiness or haze at the bottom of the test jar, the temperature is recorded as the cloud point.

To determine pour point, a sample of oil is cooled in flat-bottomed tube (*i.e.*, test jar) under specified conditions; the temperature is observed in increments of 5°F until no movement is observed at the surface of the oil when the tube is held in a horizontal position for 5 seconds. This temperature is recorded as the solid point. By definition the pour point is 5°F above this temperature.

Significance. Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines might become dogged because of wax separation. Filterability depends on type of wax, micro crystalline or amorphous. The amorphous wax is sticky in nature and would more easily clog filter screens. Pour point values of petroleum and non-petroleum lubricants are significant as many operations must function in sub-freezing conditions.

Aniline Point: Aniline point is defined as "the minimum equilibrium solution temperature for equal volume of aniline and oil sample." It is determined by thoroughly mixing equal volumes of oil sample and aniline in a test tube and heating the mixture until a homogeneous solution is obtained. Then, the tube is allowed to cool at a controlled rate. The temperature at which the oil and aniline phases separate out is recorded as the aniline point. A lower aniline point of oil means a higher percentage of aromatic hydrocarbons in it. Since aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Thus, higher the percentage of aromatic hydrocarbon or lower the aniline

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point of an oil, more are the chances of deterioration of an oil when it comes in contact with rubber sealing's, packing, etc. Consequently, low aromatic content in the lubricants or their higher aniline point is desirable.

3. Steam Emulsion Number:

When water enters an oil system, as it often does in hot strip mills, turbulence caused by high volume flow results in the formation of emulsions and initiate mixture of oil and water. Depending on the base oil and the refining processes, some oils form emulsions with water more easily than others. Moreover, contamination also contribute to the formation of emulsions. These emulsions have poor lubricating properties thereby causing abrasion and wearing out of the lubricated parts of the machinery. The higher the percentage of water, the worse the lubricating properties. Hence, it is desirable that the lubricating oil should form such an emulsion with water which breaks off readily. This ability of lubricating oil to separate from water is called Demulsibility. Oil that separates readily from water has good demulsibility. Oil that does not has poor demulsibility. The tendency of lubricant Water emulsion to break is determined by following *test*; steam at 100°C is bubbled through a test tube containing 20 mL of oil, till the increases to 90°C and the time is noted when the oil, and water separate out in distinct layers. The time in second in which oil and water emulsion separate out in distinct layers is called '**steam emulsion number**' (SEN) or '**emulsification number**'. The quicker the oil separates out from the emulsion, the lower the steam emulsion number and the better the lubricating oil for most purposes.

Significance: To avoid corrosion of polished steel surfaces like roll necks and to ensure proper lubrication, it is important to evaluate the speed of water and oil separation (demulsibility properties) of medium to high viscosity circulating oils used in rolling mills subject to cooling water contamination.

4. Neutralization Number

Lubricating Oil's acidity or alkalinity is determined in terms of neutralization number.

Neutralization number represents either the **Total Acid Number (TAN)**. "The number of milligrams of potassium hydroxide (KOH) needed to neutralize any acid in one gram of oil" or the **Total Base Number (TBN)**. The number of milligram of hydrochloric acid (HCl) needed to neutralize any base in one gram of oil. Determination of TAN is more common and its test procedure is given below:

Reagents:

- (i) 0.1 N alcoholic HCl solution,
- (ii) 0.1 N alcoholic KOH solution,
- (iii) Titration solvent: Made by mixing 500 mL of toluene and 5 mL of distilled water with 495 mL of isopropyl alcohol. .
- (iv) Para-Naphtholbenzene indicator solution made by adding 1 g of dry indicator powder in 100 mL of isopropyl alcohol.

Test procedure:

- (i) Into 300 mL conical flask, take a weighed amount of the sample (20 gm sample for light-colored oil or 2 gm sample for dark-colored oil).
- (ii) Add 100 mL of titration solvent and 30 drops of indicator solution to the flask, then carefully swirl the mixture until the sample is completely dissolved.
- (iii) If the solution turns yellow-orange or deep orange in color, it means the oil sample was acidic [But if it assumes green or green-blue color, it means the oil sample was basic, then titration should be done with HCl.
- (iv) Slowly add the alc. KOH solution from the burette drop by drop with careful swirling until the green or green-blue end point is reached which persist for at least 15 s .The color change is reversed if talc . HCl is the titrating agent].
- (v) Read from the burette the number of mL of solution required to reach the end point. ,

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Calculations: - Total mL of titrating solution / weight of sample used $\times 5.61$

Significance. This test shows relative changes in oil due to oxidation. Comparing the TAN or TBN with the values of new oil will indicate the development of harmful products or the effect of additive depletion. In fact, acid number greater than oil is usually taken as an indication of oxidation of the oil. This will consequently lead to corrosion, besides gum and sludge formation.

Saponification Number: **Saponification number** is defined as "The number of milligrams of potassium hydroxide required to saponify the fatty material present in one gram of the oil".

Determination. Saponification number is determined by refluxing a known quantity of oil with a known excess of potassium hydroxide solution and titrating the unused alkali against an acid.

Significance. Mineral oils do not undergo saponification but animal and vegetable oils undergo saponification. Hence, this test gives an indication of the amount of animal and vegetable oils added to mineral oils to improve oiliness. Moreover, most of the animal and vegetable oils possess their own characteristic saponification values. Any deviation from this value in a given sample indicates the probability and extent of adulteration. And last but not the least, this test helps us to ascertain whether the oil under study is animal/vegetable or mineral or compounded oil.

Iodine Value

The **iodine value** is defined as "the number of milligrams of iodine absorbed by one gram of the oil. It is determined by the addition of a measured, excess of a solution of iodine bromide in glacial acetic acid, to a weighed quantity of oil dissolved in CCl_4 or acetic acid. The addition of the halogenating agent to the double bond (s) is allowed to proceed to completion. The unused IBr is then back-titrated against standard hypo solution using starch as indicator.

Importance. The iodine value is a measure of the degree of unsaturation and hence the tendency of a fatty oil to absorb oxygen. Regardless of composition, any oil exposed to air and heat eventually combines with the oxygen in the air to form chemical compounds unsuitable for use as lubricants. Acids and gummy sludge are typical products of oxidation. Oils with high resistance to oxidation should be used in steam turbines and other large circulating oil systems, in which/oils attain high temperatures and remain in service for extended duration. Oils with lower oxidation resistance are satisfactory in application, where oil remains in service for periods or where makeup is high because of losses.

Carbon Residue

Lubricating oils contain high % of carbon in combined form. On being subjected to high temperatures, they decompose and form a carbonaceous deposit. There are two methods for measuring the amount of carbon residue or deposit remaining after a lubricating oil has been subjected to extreme heat.

(i) **The Conradson method.** It is conducted in the absence of air and is applicable for heavy residuals, crudes and non-volatile stock.

Procedure: A weighed amount of sample is placed in a silica crucible (of about 65-85 ml capacity), which in turn is put into a smaller iron crucible having a close-fitting cover with a small horizontal opening. The crucibles are then placed into a larger third crucible also fitted with a cover fitted loosely to shaped iron hood. Heat is supplied from a Meker burner at certain prescribed rates till vapors of all volatile matter are burnt completely. After 30 minutes the silica crucible is removed, cooled in a desiccator, and weighed.

$$\% \text{ Carbon Residue} = \frac{\text{Weight of residue in crucible}}{\text{Weight of original oil sample}} \times 100$$

(ii) **The Ramsbottom method.** This method is used with the more fluid products.

Procedure. A weighed sample is placed in a special glass bulb with capillary opening. (The oil is injected into the bulb through the capillary inlet by means of a syringe). This glass bulb containing

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sample is inserted in one of the holes of an electrically heated small furnace (Ramsbottom apparatus) maintained at approximately 550°C. At this temperature, all volatile matter escapes the bulb capillary leaving a residue that undergoes cracking and possible coke formation. After the heating, the bulb is taken out, cooled in a desiccator and weighed.

$\% \text{ Carbon Residue} = \frac{\text{Weight of residue in crucible}}{\text{Weight of original oil sample}} \times 100$

Significance of carbon-residue tests. Certain lubricating oils tend to deposit carbon in the combustion chambers of internal combustion engines, due to the carbonizing of the lubricating oil carried up past the piston rings into the combustion chambers. Incomplete combustion of fuel also results in carbon deposition. Excessive buildup of carbon deposits in the combustion chamber results in decreased volume of the charge at the end of the compression stroke giving increasing compression ratio which eventually leads to detonation. The tests are used in the evaluation of base crudes and feed stocks for the formulation of lubricants and fuels to be used in extreme temperature service.





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