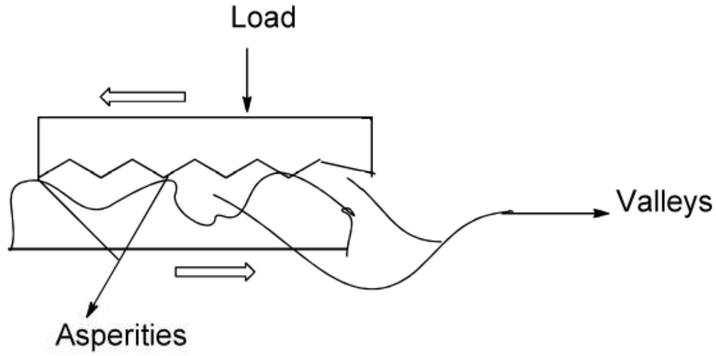
UNIT–V: LUBRICANTS AND FUEL TECHNOLOGY

Lubricants: Definition, functions of lubricants, mechanism of lubrication, classification of lubricants, properties of lubricants – viscosity, flash and fire points, cloud and pour points, Aniline points, neutralization number and mechanical strength.

All metal surfaces, no matter how smooth they are, show many irregularities in the form of peaks (asperities) and valleys. When two metal surfaces are pressed over each other, a real contact between these surfaces occurs only at a limited number of asperities. Thus the real contact is very low when compare to total surfaces. Even under low pressure at asperities may cause deformation in soft metals. In these cases two types of frictions can be observed, during the rubbing of one material over another. They are i) Sliding friction ii) Rolling friction



i) Sliding friction: If two materials of different hardness slide over one another, the peaks of the softer metal get broken more easily than the peaks of the harder materials and there is a chance for interlocking of the surface irregularities.
ii) Rolling friction can be observed when a loaded sphere or cylinder rolls over a flat surface of the other body.

The coefficient of rolling friction is very low when compare to coefficient of sliding friction, which makes lubrication is necessary in case of sliding.

A **coefficient of friction** is a value that shows the relationship between the force of friction between two objects and the normal force between the objects.

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other, as result a resistance is offered to their moment. This resistant is called as **friction**.

This friction is an undesirable process that results in (i) wear and tear of the surfaces of the moving parts (ii) loss of enormous energy as heat dissipation (iii) lowers the efficiency of the moving parts and (iv) damage of machine parts as seizure etc.

The ill-effects of the friction can be minimized by using a suitable substance, known as lubricants, which forms a thin layer in between the moving parts.

A **lubricant** is a substance introduced to reduce friction between moving/sliding/rolling surfaces. The property of reducing friction by using lubricant is known as **lubrication**.

A good lubricant possesses the following characteristics:

- High boiling point
- Low freezing point
- High viscosity index
- Thermal stability

- Hydraulic Stability
- Durability
- Corrosion prevention
- High resistance to oxidation

Functions of lubricant:

The important functions of a lubricant are

i) It prevents the direct contact between the rubbing surfaces, as a results it reduces surface deformation.
ii) It acts as coolant and prevents the chance for seizure of moving surfaces.
iii) It reduces waste of energy, so that efficiency of machine is enhanced.
iv) It avoids or reduces unsmooth relative motions of the moving/sliding parts.
v) It reduces the maintenance and running cost of the machine.
vi) It increase the efficiency of the moving parts
vii) It prevent the expansion of metal due to local frictional heat
viii) It minimize the possibility of corrosion

How Do Lubricants Reduce Friction?

Lubricants reduce friction by adding a smooth layer between two solid layers. This provides protection from damage to the solid layers. Lubricants can be used in many situations where friction is a problem.

Mechanism of Lubrication

Considering the nature of motion between moving or sliding surfaces, there are different types of mechanisms by which the lubrication is done. They are:

(i) Thick-film lubrication or Fluid-film or hydrodynamic lubrication
(ii) Thin film or boundary lubrication
(iii) Extreme pressure lubrication.

(i) Thick-film lubrication or Fluid-film or Hydrodynamic lubrication

In this type of lubrication, lubricant forms a thick layer of a fluid-film in-between the sliding/ moving metal surfaces and covers the irregularities on them, so that there is no direct contact between the material surfaces. The moving or sliding surfaces are separated from each other by a thick-film at least 1000 A^0. As a result the direct surface to surface contact and welding of junctions rarely occurs. This prevents the deformation. At this stage, the resistance to movement of sliding/ moving parts is only due to internal resistance between the particles of the lubricant moving over each other. So the lubricants having low viscosity are used in this lubrication, it is because to avoid internal frictional resistance of the lubricant molecules

Hydrodynamic lubrication is said to exist when the moving surfaces are separated by the pressure of a continuous unbroken film or layer of lubrication. In this type of lubrication, the load is taken completely by the oil film (oil layer).

The basis of hydrodynamic lubrication is the formation of an oil layer. When the normal bearing rotates, it creates oil taper between the two surfaces, and the pressure build up with the oil film supports the load. *Hydrocarbon oils* are considered to be satisfactory lubrication for fluid film lubrication. Hydrodynamic lubrication depends on the relative speed between the surfaces, oil viscosity, load, and clearance between the moving or sliding surfaces.

The thick-film lubricant / Hydrodynamic lubrication should satisfy the following conditions.

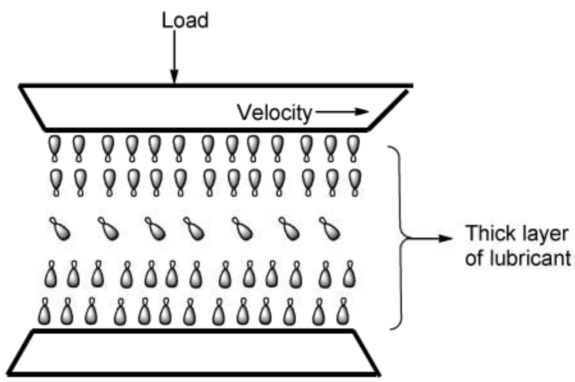
a) Should have the minimum viscosity.

b) It should remain in place and separate the surfaces. In such a case the *coefficient of friction* is in between **0.001 to 0.03.**

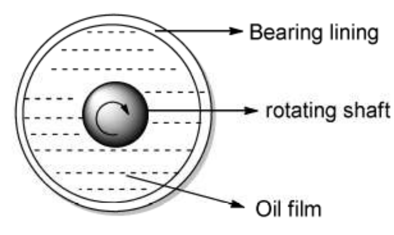
Application of hydrodynamic lubrication / thick film lubrication

- Delicate instruments & Scientific instruments.

Ex: Light machines like watches, clocks, guns, sewing machines.



Thick layer of lubrication



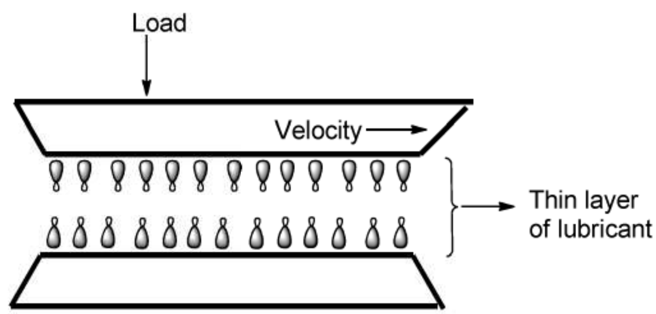
Hydrodynamic lubrication

(ii) Thin Film Lubrication or Boundary Lubrication

Boundary lubrication happens when

a) A shaft starts moving from rest. b) The speed is very low.

c) The load is very high. d) Viscosity of the lubricant is too low.



Clearly, boundary lubrication exists when the operating condition is not possible to establish a full fluid condition, particularly at low relative speeds between the moving or sliding surfaces. Here thick film of lubricant cannot be maintained between the moving surfaces but the lubricants are adsorbed physically / chemically on the metal surfaces. Under such conditions, the space between the moving / sliding surface is lubricated with oil as a thin layer. This adsorbed oil layer avoids direct metal to metal contact and further the applied load is carried by the layer of the adsorbed lubricant on the metal surface. The oil film thickness may be reduced to such a degree that metal to metal contact occurs between the moving surfaces. The oil film thickness is so small that oiliness becomes predominant for boundary lubrication. In such a case the coefficient of friction is in between **0.05 to 0.15.** The effectiveness of boundary lubrication depends on the oiliness of the lubricant. Oiliness is the ability of a lubricant to stick on to the surface.

Vegetable/Animal oils are considered to be satisfactory lubrication for Boundary lubrication. Ex: Oleic acid ($C_{17}H_{33}COOH$), Steric acid ($C_{17}H_{35}COOH$) either physically adsorbed to metal surface or react chemically at the metal surfaces and forms a thin film like a protective layer that resembles a molecular shag (carpet), which acts as lubricant.

Examples for boundary lubrication**:**

- Rollers, Gears, Tractors, Railway track joint
- Bearings, Diesel Engines, Cams
- Piston rings and cylinder liner .

(iii) Extreme Pressure Lubrication

When the moving or sliding surfaces are under very high pressure and speed, a high local temperature is attained. Under such condition, liquid lubricant fails to stick to the moving parts and may decompose and even vaporize. To meet this extreme pressure condition, special additives are added to the minerals oils known as *extreme pressure additives*. These special types of lubricants are called as "extreme pressure lubricants."

These *extreme pressure additives* are organic compounds having active radicals or groups such as chlorine, sulphur, and phosphorus. These compounds react with metal surfaces at very high temperature, pressure to form metallic chlorides, sulphide or phosphides. The formed new surface film is more durable, and capable of withstanding high loads and high temperature.

For example iron chlorides and iron sulphide can withstand up to 650 °C and 1100 °C respectively. In this way the extreme pressure lubricants serves as good lubricants under extreme pressure and extreme temperature conditions.

Difference between fluid film lubrication & boundary lubrication

Thick-film lubrication or Fluid film lubrication	**Thin Film Lubrication or Boundary lubrication**
These are used in the machines working under light load & high speed	These are used in the machines working under heavy load & low speed
Lubricants having low viscosity are used in this lubrication.	Lubricants having high viscosity are used In this lubrication
The thickness of lubricating oil film is more than 1000 A^0	The thickness of lubricating oil film is less than 1000 A^0 (~100 A^0)
Coefficient of friction is in between 0.001 to 0.03.	Coefficient of friction is in between 0.05 to 0.15.
The thick-film lubricating oil does not adsorb on metallic surfaces. i.e. They work as such.	The thin film of lubricating oil is adsorbed by physical or chemical forces at the metallic surface
The load applied is sufficient to keep apart the moving surface	The load applied is carried by the layers of adsorbed lubricants
For example: Watches, clocks, gums, sewing machines	For example: Rollers, Gears, Tractors, Railway track joint

CLASSIFICATION OF LUBRICANTS

Based on their physical state the lubricants are broadly divided into *three* types.

(I) Liquid Lubricants or lubricating oils

(II) Semi-Solid lubricants or greases

(III) Solid lubricants

(I)<u>Liquid lubricants</u>:

- Liquid lubricants reduce friction and wear between two moving or sliding metallic surfaces by providing a continuous fluid film in between them.
- They act as a cooling medium, a sealing agent, and corrosion preventers.
- Further they show thermal stability, and oxidation resistant
- Liquid lubricants are classified into many types, depending on the type of base oil used

a) Vegetable oil and animal oil b) Mineral oil (or) petroleum oil

c) Blended oil d) Synthetic Lubricants

a) *Vegetable oil and animal oil*:

(i) Before the advent of petroleum industry, oils of the vegetable and animal origins were most commonly used lubricants because of their high oiliness.

(ii) But there usage is limited due to following reasons. They i) are costly ii) undergo oxidation easily leads to formation of gummy material iii) easily hydrolyze iv) decompose at high temperature.

(iii) However, they are used as blending agents with other lubricating oils to increase their oiliness.

Oil category	Source	Application
<u>Vegetable Oil</u> i) Castor oil ii) Olive oil iii) Palm oil	 Castor seeds Olive seeds Palm fruits	▪ To withstand high speed and low pressure ▪ In watches and scientific instrument
<u>Animal Oil</u> i) Whale oil ii) Lard oil	 Whales Pig	• Light machinery lubricant • Ordinary machinery lubricant

b) *Mineral or Petroleum oils*:

Mineral oils that are used as lubricants are obtained by fractional distillation of petroleum. During fractional distillation the carbon chains with 12 to 50 carbon atoms collected separately and they can use as lubricants. Greater the carbon chain, greater the viscosity.

	Category	Carbon atoms	Use as lubricants
i	Light oil	12-20	Transformers, refrigerators, spindles
ii	Medium oil	21-30	Compressor, light machinery
iii	Heavy oil	31-40	Internal combustion engines, gear oil, heavy machinery
iv	Residue	41-50	Engines works at high lode

Asphalt (sticky, black and viscous liquid)

The mineral oils are mostly used as lubricants; because they are i) cheap ii) available in abundance iii) stable under working conditions.

However, these mineral oils as such cannot be used as lubricants, because, they contain wax, asphalt and other oxidizing compounds. So they have to be thoroughly purified before being used as lubricants. But on purification these lubricants loses some of the essential properties.

c) ***Blended oils <u>or</u> doped oil <u>or</u> compound oil*:**

The property of mineral oils can be enhanced or regenerated by adding external additives. So these are called as Blended oils.

(i) *Oiliness-carriers*: the substance added to improve oiliness of lubricant.
Eg. Animal oil (oleic acid, stearic acid) and vegetable oil (coconut oil, castor oil)

(ii) *Extreme pressure additives*: under high pressure a thick film of oil is difficult to maintain. The organic compounds with chlorides, sulphides and phosphide compounds are used as extreme pressure additives. These compounds react with metal and forms metal chlorides, metal sulphides and metal phosphides respectively. And they tolerate extreme pressure and temperature.

(iii) *Viscosity index additives*: High molecular weight compounds like hexanol, polyisobutylenes prevent thickening at lower temperature and thinning at higher temperature.

(iv) *Thickeners*: The compounds with molecular weight between 300 and 3000 (polystyrene and polyestyers etc.) are added to lubricants to increase their viscosity.

(v) *Anti-oxidants*: For retarding the oxidation in internal combustion engines, turbines etc. eg; phenols and aromatic amino compounds.

(vi) *Corrosion inhibitors*: Organic compound of antimony and phosphorus prevents the corrosion of bearings.

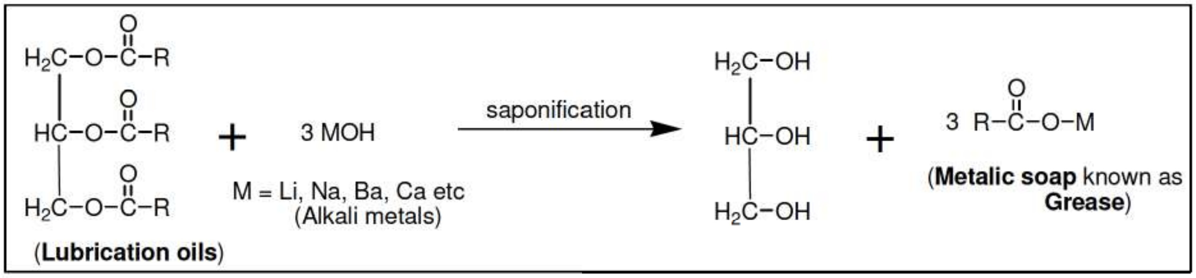
(vii) *Deposit inhibitors*: due to internal combustion engine or imperfect combustion there is chance for the deposition of carbon particles. Salts of phenols and carboxylic acids are used as deposit inhibitors.

d) ***Synthetic oils*:**

- Eg: Silicons (Si-O-Si) and polyglycol-ether (C-O-C). These lubricants work at various temperature ranges.
- The synthetic lubricants are developed to use under harsh conditions those existing in aircraft engines. In which the same lubricant has to work in the temperature range of -50 to -250 ^{o}C during takeoff and during landing the temperature stands in between 120 to 150 ^{o}C.
- Further, these synthetic oils used in rocket motors and atomic energy plants, furnace doors etc.
- Synthetic oils show following characteristic i) non-inflammable ii) high thermal stability iii) high viscosity-index iv) chemically stable.

(II) Semi-solids lubricants or Greases:

- The lubrication oils on treating with alkali gives a metallic soap called as Semi-solids lubricant. This process is called as 'saponification'.
- Additives are added to semi solid lubricant to improve its quality of Semi-solids.
- After, saponification hot lubricating oil is added to Semi-solids and stirred continuously to get greases.



Main function of Semi-solids lubricants:

i) they act as thickeners
ii) sticks to the surface of metals
iii) water and oxidation resistant

Further, the chemical nature of the metallic soap decides its property and applications.

Example	Property	Application
lithium soap	water resistant	Works at low temp (15 ^{0}C)
Sodium soap	slightly water soluble and Can with stand up to 175 ^{0}C	ball bearings
Calcium Soap	water resistant	engines working at low speed and high loads
Barium soap	water resistant but somewhat toxic	in automobiles
Aluminum soap	Water resistant, good adhesive property	in heavy duty engines, wire ropes

When the greases are used?

i) When oils are not enough to work as lubricants
ii) In bearing and gears works at high temperature
iii) Where bearing need to be sealed against entry of dust or moisture etc.
iv) Frequent use of lubricants can be avoided.

(III) Solid lubricants: Eg- graphite, molybdeniumdisulphide (MoS_2), mica (mineral silicates) etc

At normal temperature they are solid in nature. They are used when

(a) The lubricating oils and semi-solid lubricants fail to work effectively.
(b) The operating temp and load is too high.
(c) Combustible lubricants must be avoided.

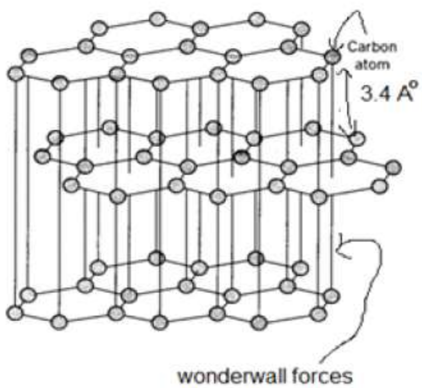
- *Graphite* is most widely used solid lubricant; due to its soapy touch, non-inflammable non-oxidized and thermal stability (up to 400 ^{0}C).
  i) The graphite is used in powdered or suspension form.

ii) When the graphite is dispersed in oil, it is called as oil-dag and when it is dispersed in water, it is called as aqua-dag.

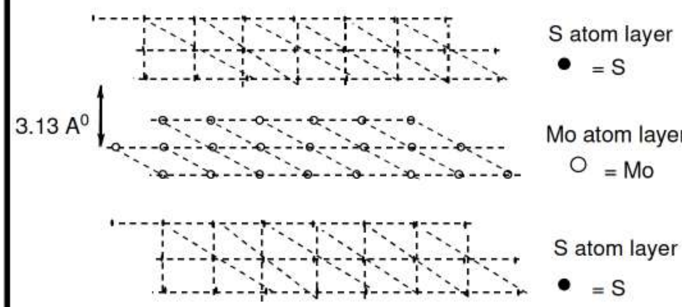
Oil-dag is used in internal combustion engines. (Where it forms a film between the piston rings and the cylinder and gives tight-fit contact)

Aqua-dag is used in air compressors, railway track-joints.

- *Graphite-greases*: Graphite is mixed with greases to form graphite-greases which can use at high temperature.
- *Molybdenium disulphide* (MoS_2) (mp.1185 °C). Possesses very low coefficient of friction and is stable at very high temp. MoS_2 can also use in powdered or suspension form. Its fine powder sprinkled on surfaces sliding at high velocities. It is also used along with solvents and greases.



Layer structure of Graphite



Sand witch-like structure of MoS_2

PROPERTIES OF LUBRICATING OILS

A large number of lubricants are available now a days and their specific application depends on the properties of the lubricant. Some of the important properties of lubricants are

a) Viscosity & Viscosity-Index **b)** flash point & fire point **c)** cloud point & pour point

d) Aniline point **e)** neutralization number **f)** mechanical strength

***Viscosity &* Viscosity-Index**:

- Viscosity is the most important property of lubricant. Viscosity describes the flow behavior of a fluid. This indicates the resistance of a liquid to flow.
- Viscosity defined as "The internal resistance offered by the fluid to the movement of one layer of fluid over an adjacent layer.
- In general liquids move like a series of parallel layers. When a series of parallel layers moving one above the other; any two layers moves with different velocity due to internal friction.
- Consider two layers of a liquid separated by a distance '**d**' and moving with relative velocity difference '**v**'. Then force per unit area '**F**' required to maintain the velocity differences is given by

$$F = \frac{nv}{d}$$ Where '***n***' is eta. Called as *viscosity coefficient*

- Viscosity is measured in terms of *viscosity coefficient*. The unit of viscosity is Poise.

  The *viscosity coefficient* is defined as "force per unit area required to maintain a unit velocity gradient between two parallel layers".

Significance of Viscosity:

- The lubricants with *low Viscosity* are applied for bearings subjected to high speed, low temperature and low pressure (sewing machines)
- The lubricants with *high Viscosity* are applied for bearings subjected to low speed, high temperature and high pressure (heavy trucks).

If viscosity is low, this results to:

- Loss of oil film causing excessive wear
- Increased mechanical friction causing excessive energy consumption and Heat generation due to mechanical friction

If viscosity is very high, this can cause:

- More stickiness results excessive fluid friction. This leads to
  - Excess energy consumption to overcome fluid friction.
  - Excessive heat generation resulting in lubricant oxidation leads to sludge formation

❖ In order to maintain the viscosity of the oil in all seasons of the year, ordinary hydrocarbon lubricants are blended with selected long chain polymers.

Effect of temperature on viscosity:

- At particular temperature, higher the flow rate, lesser is the viscosity of the oil.
- Viscosity of a lubricant oil decreases with increase of temperature and consequently it becomes thinner. On the other hand the Viscosity of a liquid increases with decrease of temperature and consequently it becomes thicker. However, the viscosity of good quality lubricant should not change much with change in temperature.
- **The rate at which the viscosity of oil changes with temperature is measured by an arbitrary scale, known as Viscosity-Index (V.I.).** The viscosity index is a unit less number.
- Higher the level of the viscosity index, the lower the variation in viscosity at temperature changes.
- The viscosity index is different for different lubricants.
- In general the Viscosity-Index of lubricating oils are improved by using external additives. Normally these additives are external organic polymers (viscosity modifiers), which are sensitive to temperature.

a) At low temperature, an external organic polymer is less soluble in lubricant oil and does not impact the fluid viscosity.

b) At high temp, external organic polymers are highly soluble in lubricant oil and as a result, the viscosity of the lubricant oil unchanged.

- The molecular structure of the lubricating oil has the direct influence on the viscosity and Viscosity-Index.
  a) Molecules of linear strictures possessing free rotation, thus shows low viscosity.
  b) The molecule with short side chains/branches exhibits high viscosity. It is because the side chains prevent the alignment of the neighboring molecules due to the greater intermolecular forces of attraction.
  c) In general lubricant with high molecular weight shows high boiling point and high viscosity.
- *Measurement of viscosity of lubricating oil*:
  i) The instrument used for measuring the viscosity is known as viscometer.
  ii) There are many types of viscometers are available. Ex: a) Ostwald's Viscometer b) Redwood Viscometer etc.
  iii) *Principle*: In any 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 proportional to the viscosity of that liquid.

Flash point & Fire point:

- *Flash point* of lubricating oil is defined as "the lowest temperature at which the lubricating oil gives enough vapors to ignite for a moment, when a tiny flame is brought near to it".
- *Fire point* of lubricating oil is defined as "the lowest temperature at which the vapors of lubricating oils burn continuously at least for 5 sec. when a tiny flame is brought near to it".
- A good lubricant should have flash-point at least above the temperature at which it is to be used and in general, the fire points are 5 to 40 ^{o}C higher than its flash points.
- Flash point & Fire point are usually measured by 'Pensky-Martens flash point' apparatus.

Fire point > Flash point > Operating temperature

Cloud point & Pour point:

- When lubricating oil is cooled slowly, the temperature at which it becomes cloudy in appearance is called its Cloud point and the temperature at which lubricating oil ceases to flow or pour is called as Pour point.
- Cloud point and Pour point of a lubricant indicates the suitability of lubricants in cold conditions.
- Pour point indicates flow characteristic at low temperature.
- Lubricant used in the machine working at low temperature should possess low pour point chance. Otherwise solidification of lubricant cause jamming of machine.

- Pour Point depends on the wax content of the oil. The presence of wax in lubricant enhances the Pour point property of a lubricant.
- The Pour point of lubricant is determined by using ‘Pour point apparatus’.

Pour point < cloud point < Operating temperature

Aniline Point:

- It is defined as “the lowest temperature at which equal volumes of fresh aniline and lubricating oil are completely miscible”.
- Aromatic hydrocarbons have a greater tendency to dissolve rubber, hence oils with a low aromatic content in lubricating oil is desirable.
- A higher aniline-point means a ‘higher percentage of paraffinic hydrocarbons’ and a ‘lower percentage of aromatic hydrocarbons’.
- Aniline point gives an indication of the possible deterioration of oil in contact with rubber sealing, packing etc.
- Therefore the oils with high aniline points are the most desirable for use in drilling fluid in order to minimize damage to rubber equipment on the rig.

Aniline point > Operating temperature

Neutralization number: (Acid number)

- It is defined as the number of milli grams of KOH required to neutralize free acids in 1 g of lubricating oil.
- A lubricating oil should possess an acid values less than 0.1%.
- The values higher than 0.1% shows that the oil has been oxidized, which leads to corrosion of machine parts in addition to gum and sludge formation.

Mechanical strength:

- The stability of lubricant under the condition of very high pressure is determined by mechanical tests.
- One of such test is ‘Four-balls extreme-pressure lubricant test’ for estimation of the mechanical strength of lubricant.
- The lubricant under-test is poured in a machine contain four balls. The lower three balls are stationary; while the upper ball is rotated. The pressure is gradually increased on the balls. If the lubricant is satisfactory under the given pressure, the ball bearing after the test comes out clean. When the load is progressively increased and if the liberated heat causes the weld the balls together, the lubricant is said to have failed completely. Thus this test helps to determine the maximum load that can be carried safely by a lubricant.