1.1 Lubricants

In almost all types of machineries, the surfaces of moving or sliding or rolling parts rub against each other. Due to this mutual rubbing between the parts, a resistance is offered to their motion. This resistance is known as friction [1]. It causes a lot of wear and tear of surfaces of moving parts. Any substance introduced between two moving/sliding surfaces with a view to reduce the friction (or frictional resistance) between them, is known as a lubricant. The main purpose of a lubricant is to keep the moving/sliding surfaces apart, so that friction and consequent destruction of material is minimized. The process of reducing friction between moving/sliding surfaces, by the introduction of lubricants in between them, is called lubrication [2].

1.2 Timeline of lubricants

The meaning of friction and resistance has been understood very practically by our civilization, the history of lubricants tell us that in order to reduce friction people have used oil or water as a lubricant at Egyptian times. It all started in ancient Egypt, with the need to move blocks for the construction of Sphinxes and Pyramids. As the lubrication theory was unknown, the Egyptians slaves used branches of trees to drag and pull sleds with approximately 60 tons of blocks. As one example, in an Egyptian tomb built around 2400 BC, the anaglyph inside recorded that people at the time used lubricant (water) to help carry the statue [3-6].
2600 B.C

The very first trace of lubrication, for reduction in friction, was found in the sledge wheel that belonged to Ra-At-Ka (King of Egypt), proved by analysis that the lubricant was beef or ram tallow. After this discovery, it was concluded that in ancient Egypt the tallow was used as lubricant under the sleds to facilitate sliding.

777 B.C – 393 A.C

At this time Greece celebrated the first Olympic Games, a tradition that continued every four years. One of the modalities of the Olympics was the chariot race, which also had the axles lubricated by animal fat.

200 A.C

At this time, the Romans also used the chariots as transportation, which were also lubricated by animal fat.

5th to 10th Century

In the Middle Ages animal fat was used sparingly to lubricate the mechanism for opening the gates of castles and on carriages wheels carrying kings and queens.

8th Century

At the end of this century, in Norway, year 780, the Vikings Warriors and Maritimes Adventurers were experts in building boats. They built the first and improved Drakkars - long sailing boats. For a long time, whale oil is been used to lubricate the sails hinge support and the rudder axis.
In the beginning of the great commercial navigation, whale oil was also used to lubricate the pulleys and rudders of ships. The Oil, mineral existing for about 300 million years, provided in the Antiquity medicinal purposes and later started to be used in lubrication. It was known as "rock oil, mineral oil and naphtha oil."

With the invention of gadgets, the need of lubricating using oil for its perfect functioning emerged.

With the civilization development and inventions even more revolutionaries, we highlight one of the greatest inventors, Leonardo da Vinci, who designed large projects that also contributed to the advance of lubrication, as the catapults, excavator, among many others.

The phenomenon of the Industrial Revolution led to the mechanization of industry and transport. With the growth of textile machinery was used lubricant for the smooth functioning of the machines.

In this century, Pennsylvania (USA) 3 important events occurred: 1) In 1859, a former American train driver, Edwin Drake, drilled the 1st oil well with 21 meters deep. Thus, it was extracted approximately 3200 liters of oil per day.
2) The need arose to lubricate the bearings of the trains, every 160km.

3) With the innovations of machinery, lubrication became necessary. After 5 years of Edwin Drake discovery, 543 companies dedicated to the extraction of oil.

20th Century.

At this time, with the 2nd World War and the need for more powerful machines and cannons, the lubricant was used in astonishing quantities. With the revolution several equipment emerged with the need of lubrication. As well as the equipment, new lubricants arise with the objective of minimizing the friction and prolong the life of equipment.

*Lubrication nowadays*

As well as the machines, lubricants suffered technological changes to meet the extreme requirements in industrial processes. Today, there are several companies in the market that manufacture various types of lubricants with mineral, synthetic and special origin. Besides having a wide use, the lubricant has a correct method of applications. For this, there are equipment for lubrication, available in Brazil since 1950, which are of fundamental use and also minimize the risk of lubricants contamination. With the global concern for the environment, various studies and researches for lubricants that could be used without harming nature were made. For this, there is lubricant used and the "green oil" which is biodegradable and an option to users to avoid more damage to the environment. Currently,
the lubrication is a decisive factor in the power of being a source of competitiveness gains, providing improvements in equipment performance, and especially the reduction in maintenance costs [7].

1.3 Role of lubricant.

The primary role of lubricants is to reduce friction between moving parts, which are in relative motion with each other. Lubrication then became the basic need for mechanical machines [8, 9]. The basic and foremost property of any lubricant is to facilitate relative motion of solid bodies by decreasing the interfacial friction and wear between surfaces. Most, although not all, lubricants are non-aqueous liquids. Owing to rapid industrialization there has been a spurt in machines, in any mechanical equipment, the moving parts or the metal surfaces come in contact but they do not usually touch over the whole of their apparent area of contact. The microscopic complex and multiplex sets of interactions are the root cause of friction and wear. When two contacting bodies are rubbed against each other, a force referred to as friction is produced at their interface which causes hindrance in their movement [10-12]. Every working surfaces are rough and this roughness on the surface creates macroscopic ridges and valleys which in turn supports friction. Lubricants constitute of more than 600 products with within a wide range of viscosities and hence the lubrication sector strives to develop various upgraded products through extensive research and development. Lubricant development is a multidisciplinary work that
includes expertise in various fields such as surface science, physics, metallurgy, chemical/mechanical/ automobile engineering, and polymer science and also requires good teamwork to make a sustainable product [13].

The tribological interactions between exposed sides with the interfacing material and surrounding system may result in loss of material from the surface. The process leading to loss of material due to abrasion is termed as wear. Wear is a process which occurs when the surfaces of engineering components are loaded together and are subjected to rolling or sliding motion. The type of friction generated during rolling or sliding motion depends upon the load and the geometry of the substrates. Wear can be minimized by modifying the surface properties of solids by one or more of “surface engineering” processes or by use of lubricants [14-19]. Lubrication is the process, or technique of reducing wear of one or both surfaces in close proximity, which are in motion relative to each other. This can be done by interposing a substance called lubricant between the surfaces to carry or help to carry the load between the opposing surfaces. The lubrication of two surfaces moving relative to each other depends upon a number of factors like load, relative velocity of the surfaces, geometry of the surfaces, physical and chemical properties of lubricants and the metals out of which the surfaces are made. The main purposes of lubrication are (i) to reduce wear and prevent heat loss that results due to contact of surfaces in motion, (ii) to protect it
from corrosion and reduce oxidation; (iii) to act as an insulator in transformer applications; and (iv) to act as a sealing agent against dirt, dust, and water. While wear and heat cannot be completely eliminated, they can be reduced to negligible or acceptable levels by the use of lubricants. Because as heat and wear are associated with friction, both effects can be minimized by reducing the coefficient of friction between the contacting surfaces. Any material used to reduce friction in this way is a lubricant [20-24]. Lubricants are available in liquid, solid, and semi-solid forms.

1.4 Theories of friction

The frictional force is the one being responsible for wear and tear of two bodies. When two bodies in contact, move relative to each other then there exists a force which has a potential to oppose that movement which is called frictional force. There are in general four different types of friction.

There are four types of friction namely

1. Static friction
2. Kinetic friction
3. Rolling friction
4. Fluid friction

1.4.1 Static Friction
Static friction comes into play when a body is forced to move along a surface but movement does not start. The magnitude of static friction remains equal to the applied external force and the direction is always opposite to the direction of motion. The magnitude of static friction depends upon $\mu_s$ (coefficient of static friction) and $N$ (net normal reaction of the body).

1.4.2 Kinetic friction

Kinetic friction denoted as $\mu_k$ comes into play when a body just starts moving along a surface. When external applied force is sufficient to move a body along a surface then the force which opposes this motion is called as kinetic frictional force. Magnitude of kinetic frictional force $f_k = \mu_k N$

Figure 1.1: Static and kinetic friction
Where \( \mu_k \) is coefficient of kinetic frictional force and \( N \) is the net normal reaction on the body. The magnitude of kinetic frictional force is always less than magnitude of static frictional force. When value of applied net external force \( F \) is more than \( f_k \) then body moves with a net acceleration and when these forces are equal then body moves with a constant velocity.

1.4.3 Rolling friction

Rolling frictional force is a force that slows down the motion of a rolling object. Basically it is a combination of various types of frictional forces at point of contact of wheel and ground or surface.

When a hard object moves along a hard surface then static and molecular friction force retards its motion. When soft object moves over a hard surface then its distortion makes it slow down.

1.4.4 Fluid friction

When a body moves in a fluid or in air then there exists a resistive force which slows down the motion of the body, known as fluid frictional force. A freely falling skydiver feels a drag force due to air.
which acts in the upward direction or in a direction opposite to skydiver’s motion.

![Diagram of forces](image)

*Figure 1.3: Fluid friction*

The magnitude of this drag force increases with increment in the downward velocity of skydiver. At a particular point of time the value of this drag force becomes equal to the driving force and skydiver falls with a constant velocity [25-30].

### 1.5 Mechanism of lubricants

When two metal surfaces come in contact with each other, bonds between atoms of both surfaces are established and adhesion takes place. If a roughness of one metal is slid across a flat surface of the other the adhesion between them can lead to transfer of material from one to the other, which is the process known as adhesive wear and is the most pervasive wear process which can never be eliminated [31]. Lubricants are applied on such working which minimizes the contact area between the metal surfaces.
The mechanism of a lubricating surface can be classified in three types

1. Thick-film lubrication
2. Thin-film lubrication
3. Extreme pressure lubrication

1.5.1 Thick-film lubrication

It is also known as fluid-film lubrication or hydrodynamic lubrication. In this type of mechanism one of the rubbing surface is slightly displaced in relation to the other and a wedge shaped film of the lubricant is formed between the two surfaces rubbing each other against each other. Thus, the pressure developed in the wedge shaped film supports the load and prevents the direct contact between the rubbing surfaces. The lubricating film fills the surface irregularities of the sliding surfaces and forms a thick layer between them. Due to formation of thick film surfaces does not come in direct contact with each other and reduces the wear considerably. The friction generated between the surfaces depends upon the dimensions of the film and the viscosity of the lubricant. The thickness of the film is about 1000 Å. In this type of lubrication the lubricant has the minimum viscosity under working condition and hence it manages to penetrate between the moving parts of metal. Co-efficient of friction in thick film lubrication lies in the range of 0.001 to 0.03.
1.5.2 Thin-film lubrication

It is also known as boundary lubrication. Such type of lubrication takes place when either a bearing suddenly comes in motion or when excessive pressure is exerted on the bearings. When two metal surfaces come in contact with the lubricant, a thin film of lubricant gets adsorbed on the metal surface and is held by Van der Waal’s force of attraction. This thin layer of lubricant prevents direct metal-to-metal contact. Friction generated in this type of lubrication mainly depends on chemical nature of lubricant and the metal surface irregularity. Co-efficient of friction in thin film lubrication ranges from 0.05 to 0.15. Lubricants used for boundary lubrication must have long hydrocarbon chain, polar groups which promotes formation of wedge in the metal surfaces. High viscosity index, resistance to heat and oxidation, good oiliness, low pour-point are the desirable properties for boundary lubrication.

1.5.3 Extreme pressure lubricants

When the moving/sliding surfaces are under very high pressure and speed, a high local temperature is attained under such conditions, liquid lubricants fail to stick and may decompose and even vaporize. When the motion of metals is subjected to constant load, a considerable amount of friction heat is generated which causes the liquid lubricant to drip out or may sometimes decompose due to high temperature. To overcome this problem some additives like organic phosphorus, sulphur and chlorinated esters are added in the mineral
These are called extreme pressure additives. These additives react with the metal surface at higher temperature to form durable films of phosphates, sulphides and chlorides which helps in reducing friction. The lubrication phenomenon is affected by through this chemical action and hence a noticeable amount of wear on the metal surfaces are expected to occur. [32-40]

1.6 Materials used as lubricants

The majority of petroleum lubricant base oils are produced through the distillation and refining of crude oil. Crude oil, extracted from the earth, is a highly complex mixture of various chemicals ranging in complexity from simple gaseous molecules to very high molecular weight components. Crude oils are primarily made of hydrocarbon, that is atoms of carbon and hydrogen bound together to form molecules of different structures [41]. Chemically crude oil based lubricants mainly consists of paraffinic and naphthenic structures, these molecules could be aromatic or polycyclic aromatic. Various types of base oils are derived from light and heavy crude, based on the type and sources where the crude petroleum is extracted. Depending on the chemical structure of base oil, base stock for lubricants are refined from crude oil to obtain products with the best lubricating properties. Base stocks generally make up 80-95% of a typical engine oil and 5% additives [42]. The physical properties of an oil depend on its base stock. In most cases it is chemically inert there are three
sources of base stock: biological, mineral and synthetic. The oils manufactured from these sources exhibit different properties and they are suitable for different applications.

1.6.1 Paraffinic Oils

Oils (alkanes) have either straight or branched structures. These oils contain waxes resulting in higher viscosity at low temperatures. During the process of refining, the normal alkanes or waxes are removed. This process is similar to winterization of vegetable oils, where the oil is cooled to the point where waxes are solidified and then filtered out. As some waxes may require much colder temperatures to solidify, some refineries are equipped to de-wax the oil by mixing the oil with a solvent. The oil is then cooled and allowed to crystallize, and the wax removed through filtration. These “deep de-waxing” processes can produce paraffinic oils with pour points down to $-30\degree C (-22\degree F)$ [43].

1.6.2 Naphthenic Oils

Oils (alkenes) have cyclic structures and are sometimes referred to as cycloalkanes. They have often six-carbon rings (sometimes five- or seven-carbon rings) and offer great solvency properties as well as cold temperature flowability [44].

1.6.3 Aromatic Oils

Oils have at least one ring of six carbon atoms with alternating double and single bonds. Most of the sulfur and nitrogen in the oil is
bound to aromatic structures; giving the aromatic oils properties that are different from the straight chain paraffinic and the cyclic naphthenic oils. When the oil has several cyclic aromatic rings adjacent to each other, it is referred to as polycyclic, as opposed to monocyclic, containing one cyclic ring. Cyclic aromatics and normal alkanes occur in oil as single molecules, while others appear in various molecular structures. Most other elements such as nitrogen, sulfur and oxygen molecules in the oils are bound to the aromatic structures. When the aromatic structures are separated from the oil, these elements, too, are removed. Each of these elements in small quantities in the oil could have some sort of impact, both positive and negative. For example, nitrogen acts as an oxidation inhibitor and as passivator for copper. Sulfur compounds provide high extreme pressure and anti-wear properties, but their presence in the oil can also cause corrosion in copper materials. Sulfur also inhibits oxidation by destroying peroxides. Oxygen dissolved in oils can accelerate oxidation, although the percentage of oxygen in fresh oil is very low. The refining of crude oil involves, through diverse methods, separating the different types of hydrocarbons from the crude oil. Simple refining can be done by merely heating the crude oil. As different hydrocarbons have different boiling points, they evaporate at different temperatures, and can be condensed and extracted. Gases such as methane may evaporate at room temperature, where as gasoline, diesel fuel, and higher viscosity hydrocarbons such as
lubricant base oils evaporate at respectively higher temperatures. The challenge for a refining operation is to control the temperatures in a way that would allow only one type of hydrocarbon to evaporate at a time for a purer product [46, 47].

1.6.4 Synthetic esters

The use of synthetic esters as high performance lubricating fluids was originally driven by the development of the gas turbine or jet engine in aviation. It was found that mineral oils and synthetic hydrocarbons did not deliver the required combination of properties, and diesters were adopted as the lubricant base fluid of choice for early aviation turbines [48, 49].

1.6.5 Vegetable oils

The advantages and weaknesses of vegetable oils for lubricant applications are well known and keeping this in focus, a lot of development and research is being done on vegetable oils to meliorate the physicochemical properties so that they may prove to be a cheap and good substitute of petroleum based lubricants. Number of plant based lubricants were developed for various sectors of industry. Vegetable oils have improved lubricity and natural viscosity, temperature properties compared with petroleum-based mineral oils. Vegetable oils in general possess high flash point, high viscosity index, higher lubricity and low evaporative losses. The presence of a polar group with a long hydrocarbon chain makes vegetable oil amphiphilic in nature, allowing it to be used as a boundary lubricant. However,
serious negative characteristics of vegetable oils are poor oxidation stability and low-temperature properties [50-54].

1.7 Classification of lubricants

Lubricants are classified into following categories.

1. Solid lubricants
2. Liquid lubricants
3. Semi-solid lubricant

1.7.1 Solid lubricants

Dry lubricants or solid lubricants are materials which despite being in the solid phase, are able to reduce friction between two surfaces sliding against each other without the need for a liquid oil medium. A solid lubricant is a material that will separate two moving surfaces under boundary conditions and decrease the amount of wear. Solid lubricants are basically any solid material which can be placed between two bearing surfaces and which will shear more easily under a given load than the bearing materials themselves. The coefficient of friction in dry lubrication is related to the shearing force and the bearing load. They are preferred where (1) the operating conditions are such that a lubricating film cannot be secured by the use of lubricating oils or grease (2) contamination (by the entry of dust particles) of lubricating oils or grease is unacceptable (3) the operating temperature or load is too high, even for grease to remain in position and (4) combustible lubricants must be avoided. They are used either in the dry powder form or with binders to make them stick firmly to
the metal surfaces while in use. They are available as dispersions in nonvolatile carriers like soaps, fats, waxes, etc and as soft metal films. Solid lubricants are either applied as surface coatings or as fillers in self-lubricating composites. The solid film lubricant provides the dual advantage of dry and clean lubrication and in many instances can replace the use of greases and fluid lubricants, particularly where slow sliding movements are involved. In addition solid film lubricants can be used in combination with fluid or pastes. Solid film lubricants enhance the lubrication of components in the boundary friction region, when there is no hydrodynamic lubrication and direct contact between the surfaces occurs. For convenience, the various types of solid lubricant are divided into various classes as follows:

(i) Structural lubricants.
(ii) Mechanical lubricants.
(iii) Soaps.
(iv) Chemically active lubricants.
(v) Development materials.

(i) Structural lubricants

This includes graphite, molybdenum di-sulphide, talc, mica, vermiculite, and also various inorganic salts which whilst proven in the laboratory are not yet extensively used in industry. These substances have, in the main, inherent lubricant properties due to their layer lattice structure and are usually anisotropic. Other structures which are known to have low shear strength have been
examined, e.g. AgCl, CuCl but whilst they all gave a low coefficient of friction for a short time, their behavior was erratic and the coefficient of friction soon increased through removal of the film. In general, lubricants in this class function by cleaving within themselves and fixing themselves on or into the bearing surface. This mechanism is discussed later in detail.

(ii) Mechanical lubricants

The main criterion of this group is their tendency to sacrificial wear and these lubricants can be divided into two groups, viz. metals and plastics. In both cases the lubricants must be capable of forming a continuous adherent film on the rubbing surfaces. This film is then worn away gradually, thus reducing the wear rate until eventually the film is removed. This mechanism is discussed in more detail under the section on plastics. The essential difference between these two groups is that the metal films in general are able to operate at higher speeds, loads and temperatures than plastic bearings.

(iii) Soaps

Soaps are used in two ways: firstly as solid lubricants in their own right, and secondly as compounds formed in situ in the metal surface by the interaction of fatty acids and the metal. Bowden has suggested that lubrication is not affected by the fatty acid itself but by the metallic soap formed as a result of chemical reaction between the metal and the fatty acid. The action of a soap is very dependent on its
melting point; this is shown quite markedly in the differing behavior of sodium and aluminum stearates. The subject is discussed in more detail under greases.

(iv) Chemically active

This category includes the E.P. additives and a variety of chemicals which are added to liquids (oils) or used in the gaseous phase and are able to interact with the metal surface to produce a lubricating layer. For example, molybdenum disulphide can be formed on a molybdenum-containing surface by interaction with hydrogen sulphide gas at about 300°C. Other chemicals used are phosphates, chlorides and oxidizing agents.

(v) Development materials

The materials in this class are still mainly in the experimental stage; most of the work is classified, as it has to do with rocketry and the defence program. However, it has been shown that combinations of various industrial refractory materials are satisfactory for short periods at high temperatures. Glass has been included in this group, but its function is entirely different as it softens at the operating temperature and assists in hydrodynamic lubrication.

Graphite and molybdenum disulfide (MoS$_2$) are the predominant materials used as solid lubricant. They can withstand temperature up to 650°C and can be applied in continuously operating situations. In the form of dry powder these materials are effective lubricant additives.
due to their lamellar structure. The lamellas orient parallel to the surface in the direction of motion. Even between highly loaded stationary surfaces the lamellar structure is able to prevent contact. In the direction of motion the lamellas easily shear over each other resulting in a low friction. Large particles best perform on relative rough surfaces at low speed, finer particle on relative smooth surface and higher speeds.

Graphite: It is the most widely used of all the solid lubricants and can be used either in the powdered form or in suspension. It is soapy to touch; non-inflammable and stable up to a temperature of 375° C. Graphite has a flat plate like structure and the layers of graphite sheets are arranged one above the other and held together by weak van der Waal’s forces. These parallel layers which can easily slide one over other make graphite an effective lubricant. Also the layer of graphite has a tendency to absorb oil and to be wetted of it.

Molybdenum Disulphide: It has a sandwich- like structure with a layer of molybdenum atoms in between two layers of sulphur atoms. Poor inter-laminar attraction helps these layers to slide over one another easily. It is stable up to a temperature of 400° C.

Solid lubricants can be applied on substrates by various methods as explained below:

**Spraying/dipping/brushing:** Dispersion of solid lubricant as an additive in oil, water or grease is most common used. For parts that
are inaccessible for lubrication after assembly a dry film lubricant can be sprayed. After the solvent evaporates, the coating cures at room temperature to form a solid lubricant. Pastes are grease like lubricants containing a high percentage of solid lubricants used for assembly and lubrication of highly loaded, slow moving parts. Black pastes generally contain MoS\(_2\). For high temperatures above 500°C pastes are composed on the basis of metal powders to protect metal parts from oxidation necessary to facilitate disassembly of threaded connections and other assemblies.

**Free powders:** Dry-powder tumbling is an effective application method. The bonding can be improved by prior phosphating the substrate. Use of free powders has its limitations, since adhesion of the solid particles to the substrate is usually insufficient to provide any service life in continuous applications. However, to improve running-in conditions or in metal forming processes a short duration of the improved slide conditions may suffice.

**AF-coatings:** Anti-friction coatings are "lubricating paints" consisting of fine particles of lubricating pigments, such as molybdenum disulfide, PTFE or graphite, blended with a binder. After application and proper curing, these lubricants bond to the metal surface and form a dark gray solid film. Many dry film lubricants also contain special rust inhibitors which offer exceptional corrosion protection. Most long wearing films are of the bonded type but are still restricted
to applications where sliding distances are not too long. AF-coatings are applied where fretting and galling is a problem (such as splines, universal joints and keyed bearings), where operating pressures exceed the load-bearing capacities of ordinary oils and greases, where smooth running in is desired (piston, camshaft), where clean operation is desired (AF-coatings will not collect dirt and debris like greases and oils), where parts may be stored for long periods of time [55-60].

1.7.2 Liquid Lubricants

Liquid lubricants prevents friction between moving surfaces by providing a film of lubricant between the substrates. These liquid lubricants are of animal or vegetable, mineral oil and synthetic sources Liquid lubricants are further classified as:

(i) Vegetable oils.
(ii) Animal oils.
(iii) Mineral oils.
(iv) Blended oils.
(v) Synthetic oils.

(i) Vegetable oils

Vegetable oils were the primary lubricants for machinery and transportation vehicles for thousands of years until the discovery of
Vegetable oils are extracted from their seeds by two methods namely solvent extraction and crushing. The extracted oil is then further purified and used for its respective purpose. Their chemical structure comprises of triglyceride of fatty acids. Vegetable oils have a property of oiliness by virtue of which they are absorbed on the tenaciously and fulfils the need of lubricant by forming a film. Research has been carried out on using vegetable oils as lubricating oil. The table below shows uses of vegetable oils as lubricants in various applications.

Table 1.1:

<table>
<thead>
<tr>
<th>Vegetable oil</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola oil</td>
<td>Hydraulic oils, tractor transmission fluids, metal working fluids, food grade lubes, penetrating oils, chain bar lubes</td>
</tr>
<tr>
<td>Castor oil</td>
<td>Gear lubricants, greases</td>
</tr>
<tr>
<td>Coconut oil</td>
<td>Gas engine oils</td>
</tr>
<tr>
<td>Olive oil</td>
<td>Automotive lubricants</td>
</tr>
<tr>
<td>Palm oil</td>
<td>Rolling lubricant, steel industry, grease</td>
</tr>
<tr>
<td>Rapeseed oil</td>
<td>Chain saw bar lubricants, air compressor-farm equipment, Biodegradable greases.</td>
</tr>
<tr>
<td>Safflower oil</td>
<td>Light-colored paints, diesel fuel, resins, enamels</td>
</tr>
<tr>
<td>Linseed oil</td>
<td>Coating, paints, lacquers, varnishes, stains,</td>
</tr>
</tbody>
</table>
(ii) Animal oils

Chemically fats and oils are the same terminology but still they differ by their thermal properties. Fats tend to solidify at 20° C, while oils remain in liquid state during same temperature range. Animal oils are extracted by rendering process. In this process the oil containing tissues are broken by treatment with steam and the oil is collected. Some common animal oils are as follows.

Whale oil is obtained by distillation of different parts of sperm whale flesh. It is thin pale yellow liquid having specific gravity of 0.88. It is used as lubricant for light machines.

Lard oil is obtained from fats, kidneys and intestines of pigs. It is colorless and used in ordinary machines for general purpose.
**Tallow oil** is obtained by compression of cattle fat under high pressure. It is used for low speed machines working under high pressure.

**Neat foot oil** is obtained by boiling foot of neat in water. It is a pale yellow liquid of specific gravity 0.915. It is used as lubricant for delicate articles such as watches, clocks, sewing machines etc. In 18\textsuperscript{th} century it was also used medicinally as a topical application for dry scaly skin conditions.

(iii) Mineral oils (Petroleum oils)

They are most widely used as they are abundantly available, quite stable and fulfil the requirements for the lubrication purpose. Chemically mineral oils based lubricants comprises of chains of hydrocarbons ranging from C12-C50. Mineral oil based lubricants are obtained by distillation of crude oil under reduced pressure. The lube fractions are obtained in three classes namely the light fraction, medium fraction and heavy fraction. These fraction of oils cannot be used as such for the lubrication purpose as they contain many impurities like wax, asphalt, various colored substances and other oxidisable impurities which needs to be removed before application. Wax interferes with lubricating properties as they tend to solidify at lower temperatures. Wax can be removed from lube fraction by chilling the oil fraction. The asphaltic impurities leaves carbonaceous impurities on the engine parts, asphaltic impurities can be removed
by extraction with solvents. The colored impurities can be removed by filtration using Fuller’s earth or activated clay. The oil has to be refined by treatment of hydrogen in presence of nickel as catalyst to remove sulfur compounds and to transform unsaturated compound into saturates. Mineral oil based lubricants are used for wide range oil application like automotive lubricants, aviation lubricants, heavy motor lubricants, hydraulic oils, tractor transmission fluids, metal working fluids, food grade lubes, penetrating oils, chain bar lubes, cutting oils, gear oils, marine lubricants etc.

(iv) Blended oils.

No single oil serves as the most ideal lubricants and hence depending on their properties and keeping an eye on application, lubricating oils has to be tailored to make them specific for desired applications. Various additives like anti-oxidants, anti-wear, anti-corrosion, extreme pressure additives etc. can be incorporated to improve their characteristics. Such type of derived oils as knowns as blended oils which confers the desired properties of lubricant required for particular machinery.

(v) Synthetic oils

Synthetic oils are easy to use under challenging conditions like high speed machineries, wide variation in temperature conditions, fire risk and heavy load. Synthetic oils performs even below -30° C and above
130° C. It is possible to synthesize lubricants with molecular structure that can cope with specific operating conditions. Dibasic esters, polyglycol ethers, fluoro and chloro hydrocarbons, organo phosphates, silicones and silicate esters etc. are currently used as synthetic lubricants. Di-esters derived from adipic and sebacic acids esterified with C8-C9 branched alcohols are used in jet engines and military equipment’s. These lubricants work over a wide range of temperatures as they have low pour point and high flash point. Phosphate esters are fire resistant and are used as hydraulic fluids. Silicates esters are used as high temperature hydraulic fluids. They have high viscosity index [61-67].

1.7.3 Semi-solid lubricants.

Greases are typically applied in areas where a continuous supply of oil cannot be retained, such as open bearings or gears. The modern definition of lubricating grease is it is a solid or semi-solid product obtained by the dispersion of a thickening agent in a liquid lubricant [68]. This system may also include other ingredients that impart special properties. Grease contains mainly three ingredients

(i) Base oil
(ii) Thickener
(iii) Additives
The majority of greases on the market are composed of mineral oil blended with a soap thickener. Most grease produced today use mineral oil as their fluid components. These mineral oil-based greases typically provide satisfactory performance in most industrial applications. The thickener gives grease its characteristic consistency and is sometimes thought of as a “three-dimensional fibrous network” or “sponge” that holds the oil in place [69]. Additives enhance performance and protect the grease and lubricated surfaces.

(i) Base Oil

Most grease produced today use mineral oil as their fluid components. These mineral oil-based greases typically provide satisfactory performance in most industrial applications. There are five specific categories of base oils. These categories define the type of base stock the oil is formulated from. The categories are as follows.

a) Group 1

Group 1 base oils are the least refined of all the groups. They are usually a mix of different hydrocarbon chains with little or no uniformity. While some automotive oils on the market use Group I stocks, it’s generally used in less demanding applications. Group I base stocks contain less than 90 percent saturates and/or greater than .03 percent sulfur and have viscosity index greater than or equal to 80 and less than 120.
b) Group II

Group II base oils are common in mineral based motor oils currently available on the market. It have fair to good performance in lubricating properties such as volatility, oxidative stability and flash/fire points. It gives fair performance in areas such as pour point, cold crank viscosity and extreme pressure wear. Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to .03 percent sulfur and have viscosity index greater than or equal to 80 and less than 120.

c) Group III

Group III base oils are subjected to the highest level of mineral oil refining of the base oil groups. Although it is not chemically engineered, it offers good performance in a wide range of attributes as well as good molecular uniformity and stability. They are commonly mixed with additives and marketed as synthetic or semi-synthetic products. Group III base oils have become more common in America in the last decade. Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to .03 percent sulfur and have viscosity index greater than or equal to 120.

d) Group IV

Group IV base oils are chemically engineered synthetic base stocks. Poly alphaolefins (PAO's) are a common example of a synthetic base
stock. Synthetics, when combined with additives, offer excellent performance over a wide range of lubricating properties. They have very stable chemical compositions and highly uniform molecular chains. Group IV base oils are becoming more common in synthetic and synthetic-blend products for automotive and industrial applications.

e) Group V

Group V base oils are used mainly in the creation of oil additives. Esters and poly esters are both common Group V base oils used in the formulation of oil additives. Group V oils are generally not used as base oils themselves, but add beneficial properties to other base oils [63, 70].

Most grease is formulated using Group I and II mineral oil base stocks, which are appropriate for most applications. However, there are applications that might benefit from the use of synthetic base oil. Such applications include high or low operating temperatures, a wide ambient temperature range, or any application where extended re-lubrication intervals are desired.

(ii) Thickeners

Lubricating greases has very complex structure and can comprise of varieties of components depending on the application [71]. Nevertheless the most important component in lubricating grease is
the thickener. The thickeners consist various metal soaps of Li, Na, Ca, Ba, Al, etc. Non-soap thickeners include carbon black, silica gel, poly-urea and other synthetic polymers, clays, etc. [72]. The primary objective of the thickener is to supply a solid structure to keep its consistency during non-operating conditions but it also provides mechanical stability to the grease both over time and under the influence of different forces e.g. shear stress [73].

(iii) Additives

Lubricating greases of today are, as mentioned before, based on scientific grounds and almost all greases contains some form of additive viz. anti-wear, extreme pressure, corrosion inhibitor, friction reducers, drop point enhancer, anti-oxidants, tackifiers etc. Additives contribute with the final touch to the grease in terms of optimal performance. The most important feature of additives are solubility and compatibility with the base oil. Depending on the compatibility the formulated grease shows the desired property. Some lubricating greases demands active additives on the metal surface to compete with polar molecules in the soap structure [61, 74].

1.8 Properties of Lubricants:

A lubricant has to meet various regimes of tribology apart from reducing friction between the moving substrates. An ideal lubricant should have following characteristics.
(i) It should have a high viscosity index.

(ii) It should have flash and fire points higher than the operating temperature of the machine.

(iii) It should have high oiliness.

(iv) The cloud and pour points of a good lubricant should always be lower than the operating temperature of the machine.

(v) The volatility of the lubricating oil should be low.

(vi) It should deposit least amount of carbon during use.

(vii) It should have higher aniline point.

(viii) It should possess a higher resistance towards oxidation and corrosion.

(ix) It should have good detergent quality.

Basically, there are two different type of lubricant parameters: chemico-physical and mechanico-dynamical. Chemico-physical tests only concentrate on certain lubricant properties, whereas mechanico-dynamical tests try to simulate the effects of load, speed, media and temperature on the friction and wear behaviour of a tribo-system. Various necessary properties to be evaluated of a lubricant before application.

1.8.1 Viscosity

It is the property of liquid by virtue of which it offers resistance to its own flow (the resistance to flow of liquid is known as viscosity). The unit of viscosity is poise. It is the most important single property of
any lubricating oil, because it is the main determinant of the operating characteristics of the lubricant. If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving/sliding surfaces. On the other hand, if the viscosity of the oil is too high, excessive friction will result [75].

1.8.2 Viscosity index

Viscosity of liquids decreases with increasing temperature and, consequently, the lubricating oil becomes 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 lubricating oil changes with temperature is measured by an arbitrary scale, known as Viscosity Index (V. I). If the viscosity of lubricating oil falls rapidly as the temperature is raised, it has a low viscosity index. On the other hand, if the viscosity of lubricating oil is only slightly affected on raising the temperature, its viscosity index is high [76].

1.8.3 Flash Point and Fire Point

Flash point is the lowest temperature at which the lubricant 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 lubricant oil burn continuously for at least five seconds, when a tiny flame is brought near it. In most cases, the fire points are 5° C to 40° C higher than the flash points. The flash and
fire do not have any bearing with 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 risk if fire, during the use of lubricant [77, 78].

1.8.4 Cloud Point and Pour Point

When the lubricant 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 lubricant oil cease to flow or pour, is called its pour point. Cloud and pour points indicate the suitability of lubricant oil in cold conditions. Lubricant oil used in a machine working at low temperatures should possess low pour point; otherwise solidification of lubricant oil will cause jamming of machine. It has been found that presence of waxes in the lubricant oil raise pour point [79].

1.8.5 Carbon Residue

The carbon residue value of motor oil, while at one time regarded as indicative of the amount of carbonaceous deposits a motor oil would form in the combustion chamber of an engine, is now considered to be of doubtful significance due to the presence of additives in many oils. For example, an ash-forming detergent additive may increase the carbon residue value of an oil yet will generally reduce its tendency to form deposits [80, 81].

1.8.6 Drop point:
Dropping point is the temperature at which the grease passes from a semisolid to a liquid state under the conditions of the test. This change in state is typical of grease containing as thickeners soaps of conventional types [82].

1.8.7 Cone penetration

In the case of lubricating greases its consistency is termed as its measure of the relative hardness or softness and has some relation to its rheological properties. A proper consistency will make the grease stay in the bearing without generating too much friction. Hardness or softness of lubricating greases can be checked using ASTM D 1403 [83].

1.8.8 Roll stability

The ability of a grease to resist changes in consistency during mechanical working is named its roll stability or shear stability. Mechanical stability is a significant characteristic of lubricating grease when dealing with the long-term service of grease-lubricated roller bearings. Consistency of greases, in service, generally decreases as it is exposed to mechanical forces caused due to churning action in rolling parts of the bearing. Poor stability will lead to degradation of the grease which results in leakage of grease through seals, or at worst a total failure of the bearing [84].

1.8.9 Wear scar

Along with a reduction in friction, wear prevention is also an important property of lubricating grease. The four-ball wear-test
method is performed to determine the wear-preventing characteristic of greases under the test conditions [85].

1.8.10 Weld load

Load is an important factor affecting the lubricant performance. Lubricant should sustain enough on the surface under high load applications, it should not squeeze out from the surface or else would cause the surfaces to weld due to extreme friction. For heavily loaded application, a high viscosity lubricant is required. The test is used to determine the load bearing properties of a lubricant at high test loads. Four-Ball Test measures a lubricant’s extreme pressure properties under “Hertzian” contact in sliding or rolling motion [86].
1.9 References


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