Chapter-1

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1. Introduction

This chapter provides a brief overview of tribology and related fields, including friction, wear, and lubrication. Further, the chapter highlights types of lubricants, liquid lubricants, and the function of liquid lubricants. In addition, the chapter explains the requirements of synthetic lubricants and provides an overview of synthetic base oils and their tribology.

1.1. Tribology

The word "tribology" was first stated in a landmark report by Peter Jost in 1966. The word "Tribology" has been deduced from the Greek word "Tribos," which means "rubbing," and suffix "Ology" means "the science of." Hence, tribology is essentially the science of rubbing. A more common tribology definition is the science and technology of interacting surfaces in relative motion and related subjects and practices [1]. Tribology is mainly concerned with phenomena related to friction, wear, and lubrication. However, Surface interactions in a tribological interface are highly complex. Their understanding requires knowledge of various disciplines, including physics, chemistry, applied mathematics, solid mechanics, fluid mechanics, thermodynamics, heat transfer, materials science, rheology, lubrication, machine design, performance, and reliability. Therefore, the knowledge of tribological phenomenon occurred at the interfaces of interacting surfaces helps reduce friction and wear in a machine and enhance the service life of machinery.

1.1.1. Friction

Friction is one of the most ancient exciting physics/mechanical engineering phenomena with significant implications on our everyday lives. Friction is defined as the resistance to motion during sliding or rolling, which is experienced when one surface, such as a solid surface, fluid layer, etc., moves tangentially over another with which it is in contact. Friction is not a material property. It is a system response. Friction can be classified into two categories: dry friction and fluid film friction [2]. Friction is essentially the result of energy dissipation at the interface, which can happen in material deformation, asperity-asperity interactions, fracture, interatomic interactions, viscous fluid film movement, etc.

1.1.2. Wear

The surface damage or removal of material from two solid surfaces in a sliding, rolling, or impact motion relative to one another is characterized as "wear." The concept of wear is commonly originated from the loss of material. However, it should be noted that damage due to material displacement on a given body (examined via microscopy) without a net change in weight or volume also comprises wear [3]. Friction is a principal cause of wear and energy dissipation. It is wrongly believed that high-friction surfaces have a high wear rate. This is not always the case. For instance, interfaces with solid lubricants and polymers offer low friction relatively but very high wear, whereas ceramics exhibit moderate friction but exceptionally low wear. According to the applications, wear can be either beneficial or detrimental. Modern research suggests that wear comprises five major and different phenomena with only one feature, i.e., the removal of solid material from rubbing surfaces. These are:

- Adhesive wear
- Abrasive wear
- Fatigue wear
- Erosion wear
- Chemical or corrosive wear

1.1.3. Lubrication

Sliding between clean solid surfaces is generally characterized by a high coefficient of friction and severe wear due to the specific properties of the surfaces, such as low hardness, high surface energy, reactivity, and mutual solubility. The enormous losses caused by friction and wear can be a significant financial burden on any national economy. The most traditional route to control these losses has been through lubrication. Lubrication is an ancient technology that spreads back to the days of the Egyptian Pharaohs, who employed animal fats and water as lubricants in constructing the pyramids. But the development and understanding of the technology were triggered between 1750 and 1850 as the industrial revolution [4]. The external substance applied between the mating surfaces is called the lubricant. Introducing a lubricant between rubbing surfaces aims to minimize the intimate contact between them and attain low friction and wear. Various lubrication regimes are defined based on the nature of the fluid film formation. These are:

- Boundary lubrication
- Mixed Lubrication
- Elastohydrodynamic lubrication
- Hydrodynamic Lubrication.

1.2. Types of lubricants

Based on the physical state, lubricants have been characterized into three different categories as follows:

1.2.1. Liquid lubricants

The liquid lubricants are also termed lubricating oils. Liquid lubricants are viscous fluids, and it is circulated through the different machine elements by using rotary mechanical systems like bearings or gears. Detailed discussion on liquid lubricants is provided in the later section of the chapter (**section 1.3**).

1.2.2. Grease (semi-solid lubricants)

Grease, also known as semi-solid lubricants, is produced by the dispersion of thickening agents in lubricating oils. Grease is a Latin word derived from Crassus, which means "fat." A standard grease comprises 5–20% thickener, 80–90% lubricating oil, and 0–10% a package of additives. The lubricating oils can be either petroleum-based lubricating oils (i.e., paraffin oil, naphthenic oil, and aromatic oil), vegetable oil (i.e., non–edible and edible oils), or a synthetic base oil of low to high viscosity, while thickening agents may be soap (i.e., Li, Na, Ca, Ba, Al, etc.) or non-soap (clay, silica, polyurea, and PTFE, etc.) [5]. The fibrous network of the thickener forms the body structure of the grease. This network restrains the lubricating oil within the voids formed between the fibrous structures. Additives are chemicals, solid particles, and fillers that are mixed into lubricants/greases to improve their physicochemical and lubricating characteristics. Commercial greases contain a package of additives such as extreme pressure (EP) agents, oxidation inhibitors, friction modifiers (FM), anti-wear (AW) agents, corrosion inhibitors, and tackiness. Compared to liquid lubricants, greases cannot effectively dissipate heat from the bearings, but they can provide an effective seal against dirt and water reaching the bearing surfaces. It can also provide a reservoir of lubricant in a bearing lubricated at long intervals. Due to higher shear and frictional resistance, the grease can support a comparatively higher load than liquid lubricants.

1.2.3. Solid lubricants

Solid lubricants and their coatings have been used by various industries to achieve low friction and high wear resistance under severe tribological conditions (such as high vacuum and/or temperature, high-speed and/or extreme loading, radiation environment) [6]. A solid lubricant is a material used as powder or thin-film, reducing friction and wear of contacting surfaces in relative motion and protecting them from damage. Currently, several types of solid lubricants can be used to control friction and wear, but the most common solid lubricants are graphite, molybdenum disulphide, tungsten disulphide, and zinc oxide. They can withstand a temperature up to 650℃ and can be applied in continuously operating situations. They are also used as additives to liquid lubricants and greases to increase the load-carrying capacity. Other solid lubricants in use are soapstone (talc) and mica.

1.3. Liquid lubricants

Liquid lubricants are widely employed in high-speed and high-load applications. A typical liquid lubricant comprises 90-95 % base oil and 5-10 % additives. Base oil is primarily composed of hydrocarbons, which provide the physical properties of lubricants, while additives offer chemical and tribological properties. A variety of approaches can be used to classify the liquid lubricants, but one of the best methods to categorize the liquid lubricant is based on the base oil used. The most common types of base oil are:

a) Mineral oil (derived from crude oil)

b) Synthetic oil

c) Biological oils (derived from plants and animals)

The performances of a liquid lubricant primarily rely on their base stock, chemical, physical and rheological properties. In addition, it also depends on the external parameters imposed, such as contact pressure, relative speed, and temperature [7]. The lubricating oils available in the market are mainly originated from three sources, as shown in **Figure 1.1**.

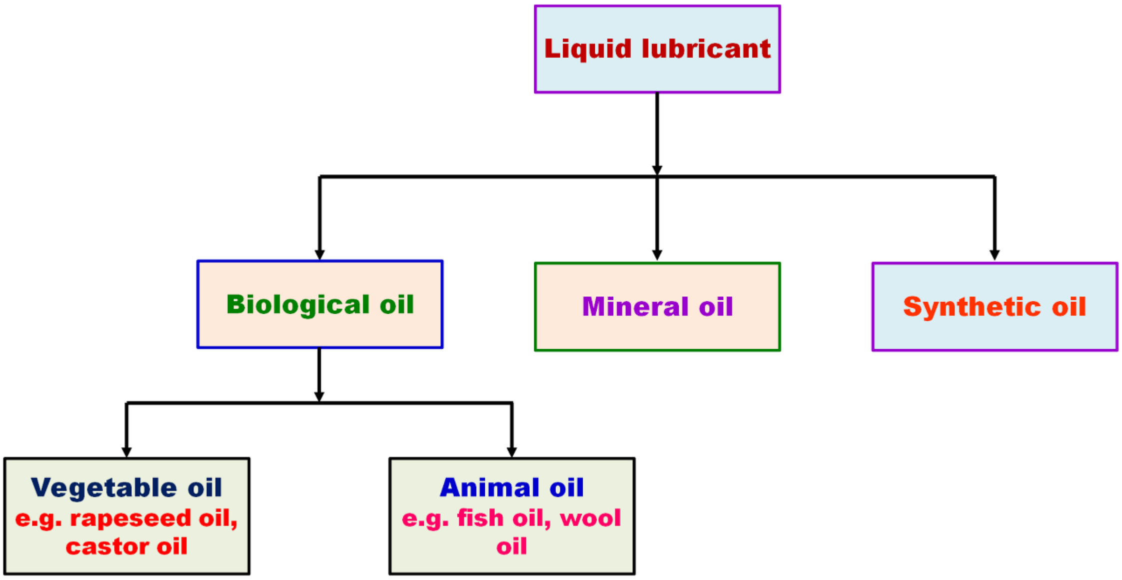


Figure 1.1: Classification of base oils on the basis of their origin

1.3.1. The function of liquid lubricants

The fundamental role of lubricants is to control friction and wear. However, it is essential to understand the role of the lubricant while choosing the proper lubricant for each application to ensure the adequate protection of any machine. The accurate understanding allows users to select the suitable lubricants, including the application method, correct quality, proper quantity, and the right time.

The roles of the liquid lubricant are divided into two categories, i.e., primary and secondary. The primary functions of lubricants are as follows:

- ***Reducing frictional effect***: - Liquid lubricant forms an oil film between the rubbing surfaces, converting dry friction into viscous friction, the most common and essential function of lubricants. Reduced friction prevents heating and abrasion on the friction surfaces.
- ***Cooling effect***: - Friction causes heating at the contact area, and more heat is produced if the matting pairs rub continuously against each other. Therefore, the heat needs to be absorbed or released. Otherwise, the system is destroyed or

deformed. It is prevented by applying liquid lubricants. To extract the heat, liquid lubricants are continuously circulated to and fro within the system.

- ***Reduced power consumption****: -:* The liquid lubricants keep the moving parts apart and allow the contacting surfaces to move freely. It minimizes power consumption, operating noise, and vibrations produced by the sliding between two friction surfaces.

The secondary objectives of liquid lubricants are stated below:

- ***Cleaning effect****:* - Lubricants maintain the engine clean by removing in-situ developed debris and foreign contamination such as dirt from the engine.
- ***Sealing effect:*** -The liquid lubricant penetrates the space between the cylinder liner, piston, and piston rings and acts as a sealing agent. As a result, gas leakage from the engine cylinder is prevented.
- ***Rust and corrosion prevention****:* - Metals produce rust and corrosion when exposed to water and oxygen. However, rust and corrosion formation can be controlled, and the system lifetime is extended if the surface of metals is coated with a lubricating oil film.
- ***Reduction of thermal stresses****:* - Lubricant also acts as a coolant. Since the rubbing of the surfaces generates local heat, which causes thermal stress inside the body, it can be avoided by applying lubricants.
- ***Load balancing****:* - Gears and bearings are limited to contacting a particular surface or line. Consequently, the load can rapidly increase, putting systems at risk of breakdown or destruction. Thus, applying liquid lubricants at the interface of friction pairs hinders the influences of increased loading by developing a thin fluid film, which distributes load within the fluid film.

1.4. Synthetic lubricants

Strict environmental regulations have directed the industry to reduce the demand for limited natural resources, reduce industrial waste and minimize hazardous emissions. On one side, numerous systems require lubrication, although, on the other side, consumption must be decreased. Therefore, synthetic lubricants were developed and used in various applications in which mineral base oils were inadequate. Synthetic lubricants are different from conventional lubricants (mineral oils) in terms of components adopted in the formulation. The synthetic base stock is the main component of synthetic lubricants. There are several definitions to describe synthetic lubricants. According to the American Society for Testing and Materials (ASTM), synthetic lubricant is a blend that contains the stocks produced by chemical synthesis and constituting essential functional additives [8]. The final base stocks are designed through molecular rebuilding by a specific chemical reaction to obtain predetermined chemical and physical properties. The benefits of synthetic lubricants are derived from the basic molecular structures and the absence of harmful molecular species often unavoidably present in conventional mineral oils in small but significant concentrations.

1.4.1. The requirement for synthetic lubricants

There are two significant rationales to use synthetic lubricants as a replacement for petroleum-based lubricants.

- When equipment requires distinct performance characteristics, such as exceptionally high or low operating temperature, stability under extreme conditions, and long service life, which cannot be fulfilled by conventional petroleum-based lubricants.

- Synthetic lubricants provide economic advantages, such as low energy consumption, high reliability, extended oil change interval, and increased power output.

1.4.2. An overview of synthetic base oils

The structural formulas of major types of synthetic base oils are displayed in **Table 1.1**. Nowadays, for lubricating purposes, the following five base oils can be commercially considered as the most significant representatives [9]:

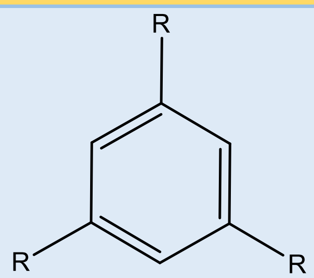
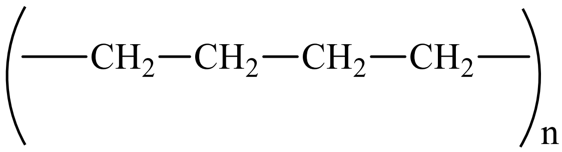
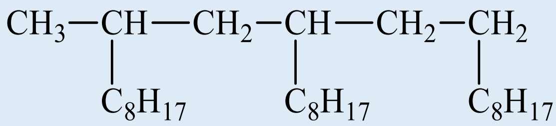
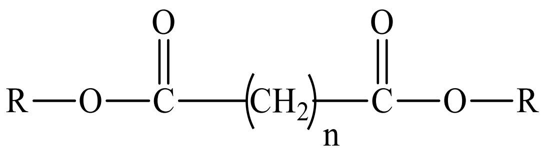
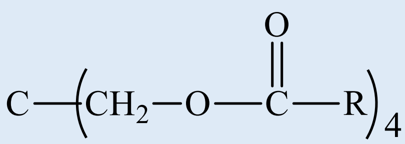
a) Polyalphaolefins (PAOs)
b) Neopentyl polyol esters
c) Polyalkylene glycols (PAGs)
d) Perfluorinated polyethers
e) Silicone oils (polysiloxanes)

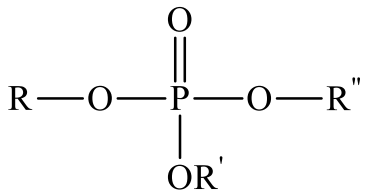
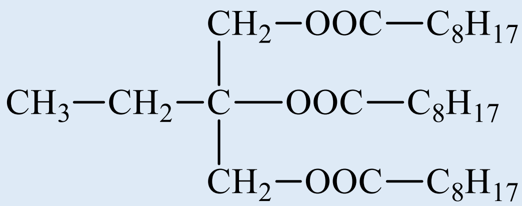
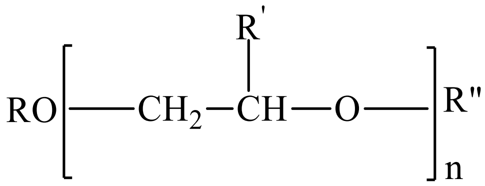
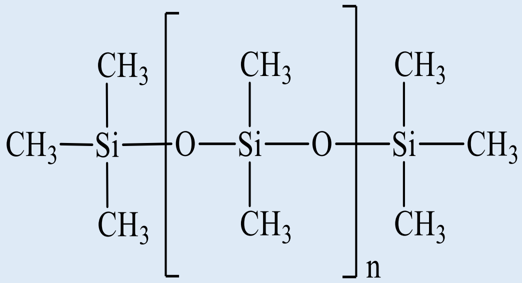
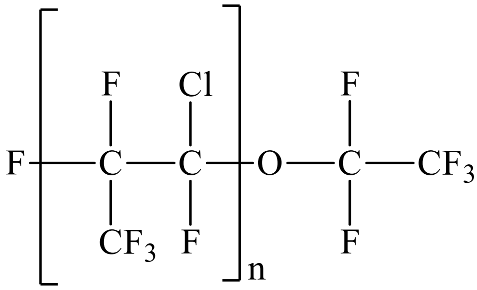
Other important synthetic base stocks are alkylated aromatics, polybutenes, phosphate ester, polyphenylene ethers, etc. Their applications are limited because of high costs or performance restrictions. It is estimated that three groups of synthetic base oils corroborate around 80% of the global market [10]. For example:

a) PAOs (45%)
b) Esters (25%)
c) PAGs (10%)

The applications of other synthetic lubricants are less compared to PAOs, ester, and polyalkylene glycols-based lubricants. For all synthetic base stocks except phosphate esters and silicones, starting ingredients are originated from basic petrochemicals such as ethylene, propylene, butene, higher olefins, toluene, benzene, xylene, and naphthalene, etc. Generally, synthetic lubricants have a high price that impacts the market expansion. The cost of synthetic lubricants can be 2-5 times higher than the cost of mineral oil-based lubricants. The value of synthetic silicone lubricants can reach up to 20 times the value of mineral oil-based lubricants. The price of lubricants plays a crucial role to opt for synthetic lubricants in developing countries, e.g., China, India, Africa, and Brazil [11].

Table 1.1: Typical chemical structures of the most common synthetic base oils [1]

S.N.	Name of lubricants	Typical structural formula
1	Alkylbenzenes	
2	Polybutene	
3	Polyalphaolefin	
4	Diester	
5	Polyolesters	

6	Phosphate ester	
7	Neopentyl polyol esters	
8	Polyalkylene glycol	
9	Silicon oils (Dimethyl siloxane)	
10	Perfluoropolyalkylether	

1.4.3. Tribology of synthetic base oils

All moving machine components rely primarily on modern lubricants for smooth and safe operation in energy efficiency, mechanical durability, and environmental compatibility. Lubricity and film strength are two factors that influence the performance of any lubricating oil. Synthetic base oils are custom-tailored, and their molecular sizes are more uniform than mineral base oils, resulting in superior film strength and lubricity than mineral oils. The film strength offered by synthetic base oil reduces the wear of rubbing surfaces under boundary lubrication conditions. Furthermore, in gearboxes, the synthetic base oils form a thin film under high-pressure conditions. As a result, the traction coefficient is reduced. PAOs and PAGs exhibit low traction coefficients as compared to mineral oils, leading to energy savings [12]. The use of an additive may further improve the anti-friction and anti-wear performance of synthetic base oils.

1.4.4. Role of additives in synthetic lubrication

It has been reported that the inherent characteristics of synthetic base oils could further be improved by using several additives such as anti-wear (AW) agents, friction reducers, antioxidants, detergents, and viscosity index (VI) improvers [13]. Among these additives, friction reducers and AW additives have evolved rapidly and attracted significant attention in recent years due to the increasing demand for fuel economy and emission reduction [14]. The prominent agents used as friction-reducing and anti-wear additives in synthetic base oils are zinc dialkyldithiophosphate (ZDDP) and molybdenum dithiocarbamate (MoDTC). In particular, ZDDP forms a protective film through complex tribochemical reactions, subject to specific operating conditions such as elevated temperature and higher mechanical shear rate. Despite their impressive tribological performance, the gas released from ZDDP and MoDTC pollutes the environment. The rapid thermal degradation of these additives results in a lack of lubrication performance during their applications [15]. Therefore, nano-additives have shown promising potential due to their inherent physicochemical properties, tiny size, dispersibility, insolubility, durability, nonvolatility, and nonreactivity with other additives. The nanoparticles have a higher surface area per unit volume as compared to the micro-sized particles. Therefore, it can smoothen and separate the mating surfaces effectively by mending, polishing, rolling phenomena, etc. [16]. The major problem with solid nanoadditives is agglomeration. Different dispersants can be used or modify the surface of nanoparticles for uniform suspension in the oil for a longer time. Importantly, different nano-additives (oxide, carbon and its derivatives, rare earth compound, polymer, etc.) behave distinctly with other synthetic oils. It indicates the importance of nanoparticle parameters like shape, size, morphology, and concentration in tribological behaviour. The detailed lubricant additive evolution and effect of nanoparticle parameters in tribology have been discussed in chapter 2.

1.5. Summary of the chapter

Although synthetic lubricant oils are more costly than conventional mineral base oils, they provide the consumer with the convenience of extended oil change intervals and higher performance, reducing friction and fuel consumption. It is projected that the demand for higher quality base oils such as synthetic lubricants will continue to increase in light of stringent engine specifications. In view of the above, the present work motivates to move towards synthetic lubrication for different tribological contact situations.