Chapter

Lubricant and Lubricant Additives

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Abstract

Lubricants have been used by humans for thousands of years in their simple machines such as wheel-axle bearings and sledges. Modern machines are much more complicated and are composed of many different machine elements which are in relative motion under varying loads, speeds and temperatures. Industrial lubricants are significant for all kinds of industries whether machine building, chemical, textile, wood, food-processing, automotive, or wind power. Today's lubricants have evolved to a complex mixture of chemical structures that ensure not only lower friction but also provide various other functionality such as lower wear, improved heat transfer, sealing, as well as control of soot, impurities, sludge and deposit formation in the mechanical equipment. Lubricant research and development has become indispensable in automotive engines and drive trains as these have been rapidly advancing towards smaller sizes, increased power, better fuel economy and lesser emissions. Development of lubricant additives and lubricant formulation has led to extended service intervals, enhanced fuel efficiency and improved machine durability. Future trends of lubricant development and use in the Industry 4.0 era and rise of electric vehicles look promising where several stakeholders already have taken their first steps.

Keywords: lubricant, lubrication, lubricant additives, base oil, greases, solid lubricant

1. Introduction

Lubricants have been in use for hundreds of centuries and are essential to our survival. Natural lubricants such as saliva and synovial fluid lubricate the food for easy mastication and reduce wear and tear of our joints respectively. Cooking oils prevent sticking of food onto frying pans and baking trays at the same time as conducting heat. Ancient Egyptians used lubricants to slide large stone blocks for building the great pyramids while the Romans used lubricant on the axles of their chariots [1]. Ancient lubricants were plant and animal based natural oils. With the onset of industrial revolution and our reliance on metal-based machinery and engines, petroleum-based lubricants witnessed a growth.

Modern lubricants are far more complex and perform various other functions in addition to lubricating such as cleaning, cooling, and sealing. The primary function of most lubricants is to reduce friction and this property is known as lubricity. A lubricant can be used in solid form, semi-solid, liquid form or gaseous form. Examples of solid lubricants are graphite and Molybdenum disulphide (MoS_2), semi-solid lubricants are greases, and liquid are automobile engine oil. Depending on the requirements of a said application, the physical state of lubricant is chosen. For example, in space environments where liquid lubrication is not feasible due to vacuum, solid lubricants are chosen. Air bearing are preferred in applications in machine tool applications where precision is of primary importance such as cutting and finishing of optical lenses. Greases are used where a liquid oil would not remain in position due to its tendency to flow or when a sealing action is needed to prevent water-ingress in addition to lubrication. Today's lubricants are designed and packaged to meet specific requirements for specific applications by lubricant formulators. The lubricant for automobile transmission and drive train has different requirements to satisfy compared to lubricant for an internal combustion engine or turbines. Further depending upon the type of turbines viz. gas, steam or hydraulic, the lubricant needs to be designed.

2. Lubricant composition

Typically, industrial lubricants contain 70-90% base oils and the rest is additives [2]. Base oils impart primary vital properties of the lubricant such as viscosity, viscosity stability, thermal stability, solvency, low temperature flow and volatility, oxidation stability. Additives have been used in lubricating oil since the 1920s and the demand for lubrication has resulted in continuous growth in the size of the market (USD 14.35 billion in 2015) with huge investments in research and development to design and formulate superior lubricants that meets present and future environmental regulations and consumer expectations. Despite this, lubricant formulation has mostly remained an art. This is because blending a new formulation for optimizing viscosity and obtaining optimum performance through performance tests for friction and emissions is much easier than testing for parameters, such as impact on engine wear, sludge build-up and piston cleanliness which require long duration engine tests. For example, during the development of Castrol's engine oil, 'Edge with Titanium Fluid Strength Technology', over 2400 unique formulations were engine-tested for an equivalent of 1.9 million miles.

To understand the need for additives, one must understand the implication of the Stribeck curve shown in **Figure 1**. Machine elements such as engine bearings work in hydrodynamic lubrication regime where the major function of the lubricant is to maintain its viscosity at all temperatures while ensuring a thick fluid film to keep the two contacting surfaces in relative motion separated at all loads and speeds. Rolling element bearings work on elasto-hydrodynamic lubrication (EHL) where the contacting surfaces deform elastically and there is a very thin film separation. Cams and tappets work in the boundary lubrication regime where there is substantial metal to metal contact. And in the reciprocating motion of engine piston rings, all four kinds of lubrication regime occur.

Classical lubrication theory assumes that a lubricating oil is a Newtonian fluid with a fixed viscosity and the contacting surfaces to be rigid. George Osborne Reynolds approached the fluid film hydrodynamic lubrication using mathematical and physical approach (1886) to predict friction, film thickness and load carrying capacity [3]. In the real world, oils undergo shear thinning and behave as a non-Newtonian fluid due to heat and pressure developed at the contact. Furthermore, real surfaces are rough and can undergo elastic as well as local plastic deformation under fluid pressure. The EHL theory was developed by H.M. Martin (in 1916) and later by Ertel (in 1939) and Grubin (in 1949), Petrusevich (in 1951), Dowson and Higginson (in 1959), Dowson and Hamrock (in 1977) for predicting traction, load carrying capacity and film thickness in heavily loaded contacts [4]. The non-Newtonian behavior of thin films under high pressure and lower rolling speeds has guided lubricant formulators to consider the shear-stress/shear-strain behavior, pressure-viscosity dependence of the lubricant as these are closely linked to the molecular properties of the oil composition. On the

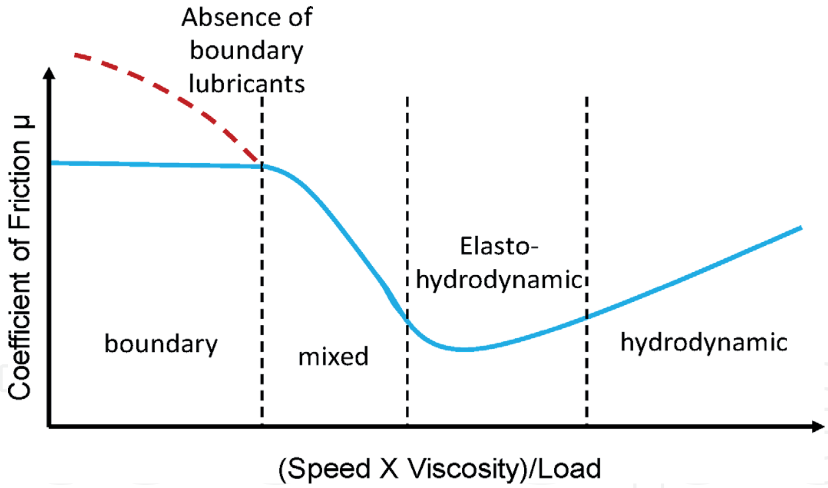

Figure 1.
Stribeck curve.

Stribeck curve, when the speed is very low, the friction is governed by the chemistry of the lubricant molecules i.e. the molecular structure and orientation. It was W. B. Hardy (in 1920), who coined the term boundary lubrication and later with Ida Doubleday (in 1922) established the basic concepts of boundary lubrication theory [5]. The boundary lubrication properties such as friction and film thickness at the interface of two surfaces are affected by the force fields of molecules in relation to their structure and polarity. Hence, formulators add boundary film additives to reduce friction in this regime [6]. Additives must also reduce wear, as in this regime, the two surfaces in relative motion are in contact hence prone to significant wear. Furthermore, additives need to counter the side effects of continuous as well as intermittent use of the lubricant such as they need to control heat, deposit formation, prevent foam formation, prevent fouling and corrosion due to water ingress, prevent wear, increase film strength under concentrated contacts, control greenhouse gas emissions. Therefore, as high as 30% content of modern automotive lubricants are chemical additives while some industrial oils may only contain 1% or less.

2.1 Base oil

A typical petroleum-based oil with no additive is called a base oil or base stock [7]. The generation of base stock starts with the identification and selection of a good petroleum crude followed by atmospheric distillation, vacuum distillation and solvent processing. Solvent processing has two processes viz. solvent extraction, and solvent dewaxing where undesirable molecules are separated where as in hydroprocessing undesirable molecules are converted to desirable ones. Hydroprocessing a general term for conversion of less desirable crude fractions into good quality feedstock using catalyst and hydrogen at high temperature and pressure. This can be categorized as hydrofinishing, hydrotreating and hydrocracking according to increasing order of severity. Another process called hydrodewaxing is required to remove long chain linear paraffins, isomerize straight chains to branched chains which improves the pour point. Only 10 % of crudes are converted to base stocks for lubricants, hence the refinery owners call the shots regarding the choice of crudes to be converted to base oils while balancing the cost, yield and demand relative to all the other refinery products. However, to satisfy lubricant performance demands under severe operating conditions, high quality base stocks are needed. The lubricant manufactures (refinery owner can also be lube manufacturer) buy these base stocks and other chemical compounds and formulate their lubricant for example SAE15W40 or ILSAC GF-5, meeting standards set by Original Equipment Manufacturers (OEMs), professional bodies, and international institutions like American Petroleum Institute (API), International Lubricant Standardization and Approval Committee (ILSAC), Society of Automotive Engineers (SAE) to name a few.

Owing their origin to petroleum crudes, lubricant base stocks are also mixtures of long chain hydrocarbons containing three types of chemical groups. i.e. paraffins, naphthenes and aromatics. The paraffins can be further classified into branched or straight chains. The chain length and branching affects the melting point and crystallization temperature of the paraffins. During the production of lube base stock, most of the unsaturated bonds, paraffin wax and sulfur content are removed, however depending on the severity of hydroprocessing, some wax, unsaturates and sulfur may remain. Base Stocks have been classified into 5 categories by the API according to the presence of saturates, sulfur content and viscosity as shown in **Table 1**. Group I, II and III are derived from petroleum crude while Group IV is reserved for Polyalphaolefins (PAO) which are synthesized from gaseous hydrocarbons. Group V is for all other base stocks that are not included in other four groups such as mineral based napthenics, synthetic esters, polyglycols, silicones, polybutenes, phosphate esters etc. These oils are designed for severe performance requirements.

2.1.1 Application based on properties of base oil

Group I base oils are processed by solvent processing in which wax and multiring aromatics are removed while some sulfur and aromatics remain. These base oils are typically used in marine and diesel engine oils, heat transfer oils, hydraulic oils, conventional greases, industrial gear oils, and machine tool oils. These oils have high solvency, very high viscosity but poor viscosity index. The maximum operating temperature is 93°C.

Group II base stocks have undergone catalytic conversion to remove wax, aromatics and sulfur compounds. These base oils are used as automotive engine oil, automatic transmission fluid, gear oils and turbine oils. The maximum operating temperature of these base stocks is 121°C.

Group III base oils are similar to Group II oils but have a higher viscosity index. The severity of hydroprocessing removes any ring structures, as a result, its solvency is poor. These base oils are used in premium passenger vehicles, automatic transmission fluids, and food grade lubricants. The maximum operating temperature is 121°C.

Group IV oils are synthetically produced Polyalphaolefins from low molecular weight organic material. They have uniform molecular structures. They provide excellent high temperature performance and oxidation stability and therefore used in high performance engine and gear applications, heavy duty industrial

	Type	Saturates (%)	Sulfur (%)	Viscosity index
Group I	Solvent refined	<90	>0.03	80 to <120
Group II	Hydrofinished	≥90	≤0.03	80 to <120
Group III	Hydrocracked	≥90	≤0.03	≥120
Group IV	Polyalphaolefins	—	—	—
Group V	Synthetics and naphthenics and other stocks not included in Group I, II, III or IV	—	—	—

Table 1.
API base stock classification.

compressor, power transmission fluid, hydraulic fluid, heat transfer fluid and in bearings as greases or liquid or lubricants. A wide range of viscosity grades of PAOs can be produced by varying the number of olefin molecules linked together. PAOs have a maximum operating temperature of 132°C.

Group V base stocks can be either naphthenic or synthetic in origin. The naphthenics provide very good low temperature performance and hence are used in applications which operate in a narrow temperature range such as transformer oil, process oils, grease. These oils have high solubility and available in a wide range of viscosities. The synthetics on the other side vary widely in their types and properties. These include polyglycols, silicones, polybutenes, organic esters, phosphate esters and they are used as compressor oils, brake fluids, heat transfer oils, aviation engine oil. Their maximum operating temperature is dependent on the nature of their molecular structure. Silicon oils are known to have a maximum operating temperature of 232°C.

Finally, Group II+ and Group III+ are two types of base stocks that are not included in the original API classification. The plus refers to increase in viscosity index (VI) in the higher limit of the API specification. Group II+ has VI minimum between 110 and 115 and Group III+ has minimum VI somewhere between 130 and 140.

As mentioned previously, mineral oils are mixtures of hydrocarbons containing paraffins, naphthenics and aromatics of various structures and carbon numbers ranging between 20 to 40+, at varying amounts depending on their degree of refining and processing. Typical composition of various API groups have been identified, but their exact structures are still not known. There is a considerable variability in the performance among the mineral origin base oils owing to the source of the crude. Therefore, lubricant manufactures conduct performance tests on their formulations to ascertain satisfactory performance with any new base stock in the same API category.

2.2 Lubricant additives

The primary function of Lubricant additives is to improve the properties of the base stock under different operating conditions and the high performance requirements of any machinery. Lubricant additives are chemical components that need to blend well with the base oil to function as a single fluid. Additive manufactures often sell several additives combined into an additive package and diluted with a base oil at a higher concentration. The additive package is then dosed into the lubricant blend by the lubricant manufacturer at an appropriate treat rate to give the desired performance. The concentration of various additives is constrained by various factors such as their primary function (for example dispersancy, wear protection and so on), their synergetic or antagonistic behaviour with other additives, and regulations set by industry bodies.

In a nutshell, lubricant additives can be categorized into various kinds based on their general roles of performance improvement and service life extension. First category are additives that impart new properties to the lubricant also known as surface protective additives. Examples include antiwear additives, extreme pressure additives, corrosion inhibitors, detergents and dispersants. The second kind of additives enhance the existing properties already present in the lubricant hence known as performance additives. Viscosity index improvers, viscosity modifiers, friction modifiers, pour point depressants belong to this type. The third type of additives known as lubricant protective additives, are the ones that counteract the negative effects or changes that take place during the service life of the lubricant. These include antifoamants and, antioxidants. In this chapter only the major types of lubricant additives are discussed. Other additives such as demulsifiers, emulsifier, biocides may be added depending on the intended applications.

2.2.1 Types of lubricant additives

2.2.1.1 Pour point depressants

As the name indicates, these are additives that reduce the pour point of the lubricant, i.e. the lubricant remains in liquid state and maintains its fluidity (pourability) at lower temperatures than without these additives. Usually as temperature decreases, paraffin molecules in the oil start to crystallize as wax (below 50°C) and the oil loses its ability to flow by gravity or to be pumped under pressure. This also affects the viscosity of the oil. Additives such as alkylaromatic polymers and polymethacrylates prevent wax crystal growth by modifying the interface between the wax and the oil molecules, to a certain extent thus lowering the pour point by about 20–30°F (11–17°C). These are present up to a fraction of a percent in all paraffin-based lubricants that lubricate machine elements such as bearings, gears exposed to cold start and cold (winter) operating temperatures. Modern multi-grade engine oils/motor oils composed of partly synthetic oil and partly mineral oil along with these additives, have pourpoints as low as −32°C.

2.2.1.2 Viscosity index improvers

Viscosity index improvers (VII) also known as viscosity modifiers are additives that prevent the oil from losing its viscosity at high temperatures which is a natural tendency of any liquid. These additives are available in all shapes and sizes and quality [8]. Polymethylmethacrylates, olefin copolymers, hydrogenated poly(styrene-co-butadiene or isoprene), esterified polystyrene-co-maleic anhydride are commonly used VIIs. The large oil soluble flexible polymer molecules uncoil and spread out as temperature increases thereby increasing the viscosity as shown in **Figure 2**. Furthermore, their numerous branches entangle with those of other neighboring molecules. By doing this, these macromolecular structures can trap and control smaller oil molecules, thus increasing the viscosity of the lubricant.

Permanent and temporary shear thinning of VII-thickened formulations can also occur depending upon the quality of the VII. In heavy duty application, due to the large compressive pressure between the two mating surfaces, VII polymer molecules, tend to align with each other and get “squashed” or even get chopped to small pieces under high shear conditions. When the polymer coils elongate and become aligned in the direction of the flow the viscosity temporarily drops resulting in reduced oil film thickness. After the lubricant leaves the contact between

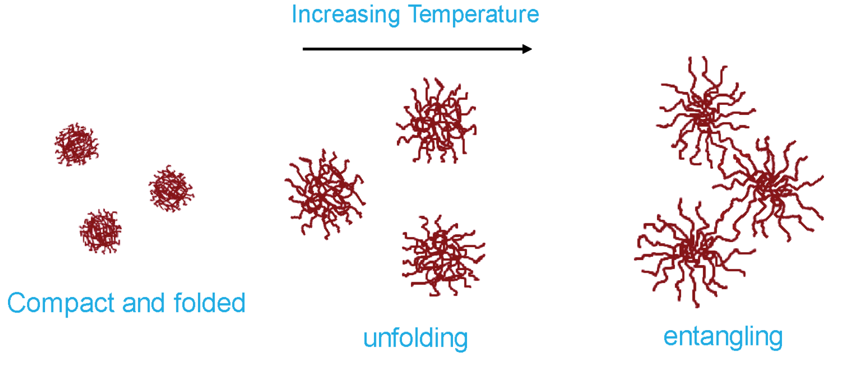

Figure 2.
Mechanism of VII.

the mating parts, the polymer coils return to their original shape and the viscosity of the lubricant returns to normal. This phenomenon is referred to as temporary shear-thinning. However, under further high shear rates, the long and flexible polymer chains can be cut or ruptured or pulled and ripped apart into smaller chains by molecular scission. Unfortunately, once this has occurred, the broken polymer chains cannot re-form into the single large chain and this causes the oil to permanently lose viscosity leading to a reduction in oil film thickness, oil film failure and an increase in wear. This phenomenon is referred to as permanent shear-thinning.

2.2.1.3 Anti-wear agent

Anti-wear additives are additives that prevent two-body wear of the metallic countersurfaces in the boundary lubrication regime where the film thickness is small and there is asperity - asperity contact. These additives are polar in nature which enables them to attach to the metallic surfaces followed by tribochemical or mechanochemical reactions to form an anti-wear film. This newly formed film undergoes wear and formation at the top layers thus protecting the underlying metallic surface. As these additives form films by chemical reactions, they get used up and the amount of antiwear additives present in the lubricant reduces with time. These are typically phosphorous compounds. Zinc dialkyldithiophosphate (ZDDP) is the most common, the most researched and has been used since the 1940s [9]. Its use has been reduced in passenger vehicles in the last decade due to zinc metal causing poisoning of the catalyst in the exhaust gas catalytic convertor. ZDDP also provide antioxidant and corrosion-inhibition properties to the lubricant. Owing to the multi functionality of ZDDP, finding its replacement has been challenging because molybdenum-based additive such MoDTC (molybdenum dithiocarbamate) or MoDDP (molybdenum dithiophosphate) molecules cannot work as antioxidant. On the other hand, ash-less antiwear additives such as hindered phenols and amines are very expensive and are required in larger quantities. Till date, ZDDP is considered as the most cost-effective antioxidant and antiwear additive available, and the alternatives are currently very expensive.

2.2.1.4 Antioxidants

Antioxidants or oxidation inhibitors prevent the oxidation of the components of the base oil there by increasing the life of the lubricant. Oxidation of the lubricant molecules occur at all temperatures but at higher temperatures, it is accelerated. The presence of wear particles, water, and other contaminants also promote Oxidation of the lubricant molecules which then leads to formation of acids and sludge. The acids may further cause corrosion in the metallic parts while the sludge formation increases the viscosity of the lubricant. Almost every lubricating oil and grease contains antioxidants and examples include Zincdialkyldithiophosphates, hindered phenols, sulphurized phenols, and aromatic amines. These compounds decompose peroxides and terminate free-radical reactions that occur in the lubricant. These are sacrificial in nature hence their quantity gets reduced with time.

2.2.1.5 Defoamants

Defoamants or antifoaming agents are additives that prevent the lubricant from forming a foam and speed up the collapse of the foam if it does form. Foaming occurs because of constant mixing of the oil with air or other gases leading to air entrapment. Foam disrupts cooling of parts as it is not a good conductor of heat. It reduces the load carrying capacity and the lubricant flow leading to excessive engine wear. Silicone polymers such as polymethylsiloxane at a few parts per million and organic copolymers such as alkoxy aliphatic acids, polyalkoxyamines, polyethylene glycols, and branched polyvinyl ethers, at higher concentration are widely used in mineral oils. The antifoaming agents are essentially insoluble in the lubricant hence they need to be finely dispersed in the lubricant. These droplets attach themselves to the entrapped air bubbles and aid in forming bigger bubbles (via coalesce). The larger bubbles rise readily to the surface followed by bursting to release the trapped air. Bursting occurs by thinning of the air bubble film as the additive spreads due to its low surface tension.

2.2.1.6 Friction modifiers

Friction modifiers are used in engine oil and transmission oil to alter the coefficient of friction that would be experienced between the sliding parts when only the base oil is present. Friction reduction results in improved fuel economy. Organic and sulfurised fatty acids, amines, amides, imides, high molecular weight organic phosphorus and phosphoric acid esters are added to the range between 0.1 and 1.5% in finished lubricants as friction modifiers. Glyceryl monooleates and Molybdenum compounds such as MoDTC and MoDTP also function as friction modifiers. They preferentially adsorb very strongly on to the metallic surface. The head of the friction modifier is attracted to the metal surface and the long tail with at least 10 carbon atoms remains solubilized in the oil as shown in **Figure 3** [10]. The chemical structure and the polarity of the molecules play a major role in the friction reduction. Ionic lubricants [11], a class of ionic liquids that are room-temperature molten salts consisting of cations and anions are also very good surface additives. The polarity of head group provides for strong surface adsorption. The physical, chemical and tribological properties of ionic liquids can be tailored to suit a wide variety of applications ranging from its use as polymer brushes in biological application, or as water soluble or oil soluble lubricant additive.

2.2.1.7 Detergents

Detergents keep surfaces free of deposits and neutralize corrosive acids formed due to oxidation. These molecules are chemical bases consisting of a polar substrate and a metal oxide or hydroxide [12]. Metallo-organic compounds of calcium and magnesium phenolates, phosphates, salicylate and sulfonates are recommended. Overbased detergents are used in marine engine lubricants to neutralize large amounts of acidic components produced by fuel combustion or oil oxidation. Ash (burning of organometallic species) and soot particles (largely carbon with sulfur adsorbed) is formed by burning of the oil in internal combustion engines. Ash can then form unwanted residues at high temperatures or simply deposit on surfaces. The deposit precursors particles are insoluble in the oil and have greater affinity for detergent molecules. The additive molecules cling to the surface of the particle and envelop it thereby also acting as dispersants and prevent those particles to agglomerate and to later settle as deposits. A detergent additive is normally used in conjunction with a dispersant additive.

2.2.1.8 Dispersants

Dispersants are used mainly in engine oil along with detergents to keep engines surfaces clean and free of deposits [12]. Dispersants keep the insoluble soot particles and the precursors of deposits in the internal combustion engine finely dispersed or suspended in the lubricant even at high temperatures. These suspended particles are subsequently removed by oil filtration or oil change. Thus, dispersants minimize damage to engine surfaces and formation of high temperature deposits. Generally,

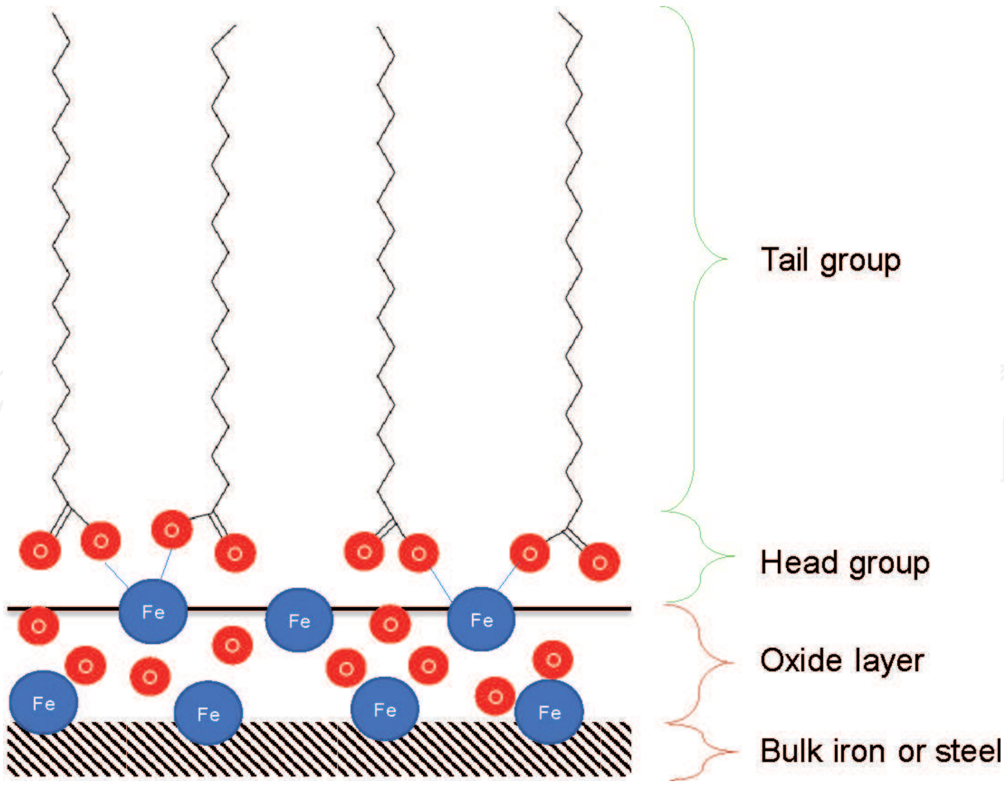

Figure 3.
Adsorption of polar headgroups onto metallic surface.

polymeric and ashless dispersants are used today such as polymeric alkylthiophosphonates, alkylsuccinimides, succinic acid esters/amides, and their borated derivatives as well as organic complexes containing nitrogen compounds.

2.2.1.9 Corrosion and rust inhibitor

Corrosion and rust inhibitors are additives that reduce or eliminate rust (corrosion of iron and steel) and corrosion by neutralizing acids and forming a protective film, either adsorbed or chemically bonded on the metal surfaces. Preferential adsorption of polar constituent on metal surface forms the protective film that prevents corrosive materials such as organic acids from reaching and attacking the metal. These are usually compounds having a high polar attraction towards metal surfaces such as succinates, alkyl earth sulfonates, metal phenolates, fatty acids, amines as well as zincdithiophosphates. Some of these inhibitors are specific to protecting certain metals. Hence, an oil may contain several types of corrosion inhibitors.

2.2.1.10 Extreme pressure (EP) additives

Extreme Pressure additives are required to reduce friction, control wear and prevent severe surface damage in heavy duty application of gears and bearings at high temperatures and pressures. They are also known as antiscuffing additives. They react chemically with metallic surfaces to form a sacrificial surface film that prevents the welding and subsequent seizure of asperities at the metal-to-metal contact. Additionally, they contribute to smoothing of the surfaces as these are formed at contact asperities and the load is then distributed uniformly over a greater contact area, thus reducing the severity of wear and ensuring effective lubrication. Effectiveness of EP additives relies on their reactivity and their ability to readily form thick surface films at high loads and high contact temperatures that are created at the mechanical contacts. These additives usually contain sulfur and phosphorus compounds and chlorine or boron compounds. Ashless EP additives such as dithiocarbamates, dithiophospates, thiolesters, phosphorothioates, thiadiazoles, aminephosphates, phosphites may be preferred in some applications where chlorine may cause corrosion.

Other additives such as demulsifiers, emulsifier, biocides are added to meet specific requirements. Emulsifiers are used as a binder between oil and water molecules in oil-water-based metal-working fluids to help create a stable oil-water emulsion. Without the emulsifier, oil and water will separate out from each other due to differences in specific gravity and interfacial tension. On the other hand, demulsifiers are used to separate oil-water emulsions. Demulsification and removal of the aqueous phase from the oil-based lubricant minimizes harmful effects such as corrosion, foaming and cavitation from occurring. Biocides may be added to water-based lubricants to control the bacterial growth.

2.3 Greases

Lubricating grease are a class of lubricant that do not flow like a fluid but bleed (release oil) when squeezed between contacting surfaces. They have a gel like consistency and can be described as a solid or semifluid like material and in some cases can be used in vertical or overhead applications because they can have good drip resistance due to their Non-Newtonian rheological properties. They are particularly useful in applications that are sealed for life; for example bearings and remote gearboxes. Functionality of greases include sealing out contamination and water ingress, prevent corrosion, compatible with polymers and elastomers, provide antiwear and extreme pressure load protection while reducing friction. Greases have three main components: fluid, thickener and additives [13].

A typical grease consists of 75-95% fluid base stock, 2-25% thickener and 0-25% additives. The base stock is chosen based on the required applications. Hence, the fluid can be petroleum based for most automotive and industrial application, synthetic based for low and high temperature application or may be wax based (no flow) for high load caring capacity. The thickeners are metal soaps which are created using the fundamental reaction of an acid and a base. Calcium based soaps have been the simplest and earliest used thickeners with a maximum operating temperature between 60 and 70°C. In the last decade, calcium sulfonate greases, polyurea greases, aluminum complex greases, lithium complex greases, sodium complex greases, and clay-based greases have received general acceptance due to their higher service temperatures of more than 150°C. However, each having their own set of pros and cons. For example, calcium-based greases do not perform well over a wide range of temperature, sodium based have deteriorated performance in the presence of water. Clay and polyurea based greases are used for high temperature (service temperatures of 190-220°C) and application that have limited relubrication access. The third component of greases are additives. Commonly used additives are listed below.

- Antiwear additives
- Antioxidants
- Extreme Pressure additives
- Friction Modifier
- Rust and corrosion inhibitor

- Tackifiers (adhesive agents)
- Odorants (perfumes)
- Dyes

Tackifiers are additives that increase the adhesive property of the grease or the lubricant. They prevent the lubricant from flinging off the metal surface during rotational movement. To be acceptable to the manufacturers and the end users the greases must be free of offensive odor and have a desirable color. Therefore, odorants and dyes are added to the grease. Although these have little effect on the grease performance, their appeal to senses has an impact on the product selection.

Greases have the unique ability to incorporate liquid as well solid additives. Solid additives such as molybdenum disulphide (MoS_2), graphite, hexaboron nitride and polytetrafluoroethylene (PTFE) in the form of fine dispersed powder (nano and micro particles) have been used in lubricants and greases to provide ultralow friction and wear protection. Solid additives provide a physical separation between two contacting surfaces when fluid is unable to provide load support. The lattice structure of these solid lubricants plays an important role in transferring a thin low shear layer on the metal surfaces especially where load is high, and speed is low.

2.4 Solid lubricants

Solid lubricants on their own are vital to niche applications such as space missions, satellites release and deployment mechanisms. Vacuum and microgravity of space eliminates the use of liquid lubricants. The importance of a thin film of solid lubricant can be emphasized on the fact that the success of an entire mission can be compromised if the, receiver and transmitter antennas or solar arrays packed securely during launch fail to release smoothly with precision due to extreme friction of a deployment mechanism. Solid lubricants can be used at low temperatures as well as at high temperatures where the liquid lubricant may solidify or vaporize respectively. Even at extreme pressures where liquid lubricant will be squeezed out, solid lubricants are used. However, solid lubricants are not limited to extreme conditions [14]. A wide variety of low friction coatings are used in various engineering applications that require high electrical and thermal conductivities, low wear rates and high lubricity at all operating temperatures. Newer engineered coatings have increased complexity and have transitioned from single or multi component structures to nanostructured and functional gradient structures.

2.4.1 PTFE

The most recognized polytetrafluoroethylene (PTFE) coating is Teflon® discovered in 1938 at DuPont. These are highly linear fluorocarbon molecules. They offer a low friction surface with moderate wear. They have low chemical reactivity and low surface energy. PTFE on its own performs best at low loads and wears rapidly at higher loads; hence they need reinforcements to increase strength and load bearing capacity. Such materials are called composite materials.

2.4.2 Carbon based materials

Carbon based materials such as graphite in both micro and nano forms is a popular solid lubricant additive whereas diamondlike carbon (DLC) makes excellent low friction coatings. However, they have different mechanisms of friction reduction. Graphite has hexagonal crystal structure which has the intrinsic property of easy shear. DLC exhibits high hardness and low friction due to an amorphous structure that combines graphitic and diamond phases. They can be doped with hydrogen or nitrogen for achieving desirable properties. Recently, a series of patents on superlubricity of nano-diamonds and graphene films have been filled [15].

2.4.3 MoS_2

Molybdenum disulphide are transition-metal dichalcogenides like Tungsten disulphide (WS_2) work on the mechanism of interlamellar shear between covalently bonded hexagonal basal planes like that of graphite. Their performance is affected by moisture content [16].

Apart from the advantages mentioned earlier, solid lubricants also have a few disadvantages. They have less ability to carry away heat and contaminants away from the contact. They have poor self-healing properties, and they are not easily entrained into tribological contacts.

3. Application methods

After the selection of a suitable lubricant, its application method i.e. its delivery to the mechanical components such as gears, bearings, cams, tappets, chains, guideways and couplings of a machine or engine in correct quantity is considered. Liquid lubricants are applied to the machine elements by two methods. First type is called 'all loss method' while second type is called 'reuse method' [2]. In all loss method a small quantity of lubricant is applied periodically and the lubricant after use, gradually leaks away to waste. In reuse method, elaborate lubricating systems are designed to feed the required quantity of lubricant to various machine elements of the system. The lubricant after leaving the machine components is collected, cooled then filtered and recirculated to lubricate the machine components again. Most open gears, ropes, guideways, chains and rolling element bearings (except sealed for life rolling element bearings) are lubricated by all loss method. Nearly all grease lubricated elements also are lubricated by this method. Some devices used for all loss lubrication method include hand-held oiling device, grease gun, drop feed cups, wick feed cups, wick oilers, pad oilers, mechanical force feed lubricators, airline oilers and automatic or semiautomatic spray units. Reuse method of lubricant application has the oil circulating through a network of pipes that is pressurized by a pump or aided by gravity. However, closed oil sump systems employ splash oiling, bath oiling or ring oiling methods. Centralized lubricant application systems can reduce the quantity of lubricant usage as well as labour costs. Automobiles use an oil mist lubrication system to lubricate various machine elements of the engine and drive train. Considerations with regards to the lubricant characteristics and composition are required while designing a compatible system. Oil condition monitoring and routine checks are vital for the longevity of the machine elements lubricated by any method.

Solid lubricants on the other hand are applied as powder dispersed in a liquid lubricant or in a solid phase matrix. They can be also applied as a thin film coating. The coatings are made by various methods such as dip coating, thermal spraying, and cold. More robust ways of coating includes chemical vapor deposition or physical vapor deposition methods. Electrochemical processes are used for producing coatings of polymer-based solid lubricants and their composites.

Physical and chemical characteristics	Performance test evaluation	Engine test evaluation
Color	Oxidation Tests	Oxidation stability and bearing corrosion protection
Density and API gravity	Thermal Stability	Single cylinder high Temperature tests
Carbon Residue	Foaming Tests	Multi cylinder high temperature tests
Flash point	Corrosion and Rust Protection Test	Multi cylinder low temperature tests
Neutralization Number	EP and Antiwear Test	Rust and corrosion protection tests
Total Acid Number	Emulsion and Demulsibility Test	Oil Consumption rates and volatility
Total Base Number		Emission and protection of emission control systems
Pour Point		Fuel Economy
Sulphated Ash		
Viscosity		
Volatility		

Table 2.
Evaluation techniques and testing.

4. Lubricant analysis

Lubricant analysis primarily refers to the characterization and evaluation of the lubricant for various physical, chemical and performance properties in all stages of its life cycle. For solid lubricants and coatings, the analysis includes determining the composition and structure by using a range of spectroscopic and microscopic observation methods as well as measuring the coating consistency and thickness applying non-destructive evaluation techniques. Standardized tribological lab tests are used to evaluate their performance. Once a candidate material is identified, larger-scale bench testing, such as engine tests, are conducted.

For liquid lubricants, characterization is done to a much larger extent due to the large variety of applications and the implication of chemistry of the formulated oils on the machine elements performance and the overall performance of the entire equipment/machine or engine. The lubricant analysis can be classified as physical and chemical characteristics evaluation, Performance test evaluation and Engine Test evaluation as summarized in **Table 2** [2]. Additionally, end users also develop their in-house in-service lubricant analysis to monitor and maintain the condition of the lubricant. The objective of such analysis is to ensure optimum performance, achieve expected life of the equipment as well as the lubricant flowing through it.

5. Future trends

Current automotive lubricants are optimized for internal combustion engines and drive trains. Electric vehicles (EVs) which use electric motors possess new challenges of lubrication such as high-power density of the small gear box which require efficient cooling. Hydro lubricants and synthetic gear oils are excellent candidates for such application but may pose sealing issues which requires innovative solutions. Lubricants are also required in the rolling element bearings of EVs that must stop electro-erosion caused by high frequency high energy discharges by being conductive. Ionic liquids are having shown good performance in preventing built up of potential [17].

The future for lubricants formulation, manufacturing and end-use is oriented towards efficiency in terms of cost and time, customized and optimized for each individual tribo-system and run reliably for even longer drain interval time. New industrial lubricants must meet stringent regulations and guarantee ecological sustainability, and climate change actions. Hence, new lubricants will contribute to 'Green Tribology'.

Tribology of lubricants plays a significant role in technology and economics of industrial development. As the fourth industrial revolution 'Industry 4.0' (combines automation with the internet of things) is in progress, several concepts can be extended to lubricant and lubricant additive development and evaluation. For example new electronic smart sensors can be used for lubricant analysis and condition monitoring. The information of various performance parameters can be stored as data and transferred to the stakeholders and decision-making points using the information and communication technologies involved in Industry 4.0. such as internet and wireless connections to and via several electronic devices. Continuous monitoring can also aid in corrective measures. In-service lubricant performance testing and evaluation generates big quantities of data from various equipment and sensors. Therefore, 'Big Data' concepts can be applied in several ways. One such example can be combining lubricant data with machine data, another can be correlation study of amount of soot produced, change in oil viscosity, friction, wear of an engine. The benefits of Industry 4.0 include shorter lubricant development time, reduced number of trials, lubricant performance prediction through chemical and physical modeling and simulations. This will transform product development process from being empirically driven to using data and simulation driven approach.

6. Conclusion

Lubricants are vital for the tribological life of the machine elements. As modern machine elements are required to perform in heavy-duty applications in a wide range of environments, newer, better and environmentally sustainable lubricants are required to be designed. Lubricant additives are therefore considered as lubrication engineering design components. Lubricant additives are designed and optimized to meet the performance requirements of the equipment or engine. Various types of lubricant additives and their functional properties were discussed. They are designed to provide oxidation resistance, high temperature viscosity, energy and fuel efficiency among others. Lubricant or grease therefore are a complex mixture of several components blended carefully together to meet the performance requirements. The different components can have synergistic or antagonistic effects due to chemical interactions or competition at the metal surface or among themselves. Therefore, formulation of lubricants requires considerable expertise and expensive performance testing. Green Tribology and Industry 4.0 era will steer the lubricant development, use and disposal.

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